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THE INSTITUTE OF PETROLEUM

AN Ordinary General Meeting of the Institute of Petroleum was held at 26 Portland Place, London, W.1, on 11 November 1953, the Chair being taken by Dr E. B. Evans, a vice-president.

The General Secretary read the minutes of the previous meeting, which were confirmed and signed as a correct record. He then read the list of members elected since the previous meeting and various announcements.

Dr E. B. Evans, introducing the author of the paper to be presented, said: The subject of our paper this evening is, as you know, Paint in the Petroleum Industry, a subject of very great importance to the industry, which spends an enormous amount of money every year in the protection of its property. The paper is being presented by Dr Footner, who is, of course, very well known to many of you. Dr Footner was educated at London University and joined the Shell Company about twenty-five years ago. For the past twenty years, he has been very intimately connected with paint and corrosion problems, and I am sure that we could have no one better able to present to us a paper on this subject. I have pleasure in asking Dr Footner to give us his paper.

PAINT IN THE PETROLEUM INDUSTRY

By H. B. FOOTNER *

THE petroleum industry is interested in paint from several points of view. It is an essential material which must be used in all branches of the industry for the maintenance and decoration of property and as a means of advertising. The industry is also interested as a producer of some of the raw materials for paint, notably white spirit, bitumen, and naphthenic acids from the conventional refining processes, and solvents and resins from the petrochemical industry.

This combination of interests makes the subject of paint a particularly important one, and its importance is emphasized by the fact that the annual expenditure on paint incurred by a large petroleum company with world-wide interests amounts to many hundreds of thousands of pounds.

The main function of a paint specialist employed by a petroleum company is to ensure that efficient maintenance and decoration are carried out in the most economical way. It must always be remembered that paint has limited uses and provides a coating which is not permanent but has to be renewed at some time or other. The use of paint must, therefore, be set off against more permanent methods of obtaining the same ends; for example, one must consider the economics of using stoved porcelain enamelled plates or coloured plastics as against panels painted with enamels for advertising or distributing facilities and, in the maintenance of plant, the economics of using special alloys or metal coatings must be compared with the use of conventional paints.

The normal thickness of a coat of paint is one-thousandth of an inch, and the film is based on an organic binder which is subject to oxidation. It will be appreciated therefore that paint is not a suitable material to prevent the type of chemical corrosion which may occur in refinery processing. Certain types of paint have high chemical resistance, and there are possibilities of using these on internal surfaces of storage tanks or other containers.

Except under very corrosive conditions paint is usually the most economical and suitable material to use on external steelwork, and generally speaking the improvement in paint quality which has taken place during the past few decades has kept it well in the picture compared with other protective processes.

In the matter of the economics of painting there are a number of factors which must be considered.

In decorative or maintenance painting the cost of labour is generally three to five times the cost of the paint used. Since 1938 the cost of paint as represented by the normal types used in the petroleum industry has quadrupled. The use of the correct types of paint may greatly increase the serviceable life in comparison with grades of lower first cost. The value of even the best paints can be greatly reduced if the surfaces to which they are applied are not properly prepared.

The consideration of these different points leads to the conclusion that for economical operation the quality of the paint must be controlled, correct methods of application and preparation must be used, and the paint must be in good condition when applied.

Control of Paint Quality

In the petroleum industry paint is used for many varieties of work, and it is necessary to use a suitable grade for each purpose. The ideal would be to employ one type of paint which would serve all purposes and could be used for steelwork, houses, drums, and so on. The nearest approach to this ideal is with air drying alkyd paints, but it is still not quite economical or feasible to use this one type for all work. It is a mistake to carry an excessive number of grades of paint. If a number of grades differing slightly in properties are carried they may, theoretically, give the best results, but in practice it is usually found that a particular type is not used for the purpose originally intended.

To obtain efficient control of paint quality it is necessary to use specifications to indicate to the manufacturers precisely the type required and in-

* The Shell Petroleum Co. Ltd.

cidentally to avoid cut-throat and unfair competition which leads to price cutting and poor quality. Buying specifications should certainly not aim at teaching a paint manufacturer his own job, but should be sufficiently complete to ensure that the desired quality is obtained.

It is considered that specification requirements should be based on the physical properties which are needed in the paint film, and should include sufficient formulating detail to ensure that the desired grade is obtained. As an example, experience has shown that the most lasting type of aluminium paint on storage tanks is one in which the binder is of the very long oil type. It is therefore necessary to specify a maximum amount of resin which is to be used in the paint medium. At the same time one knows that better service is obtained by using 25 per cent of aluminium pigment in the finished paint; therefore this quantity is specified as a minimum. These important details indicate precisely the type of paint required, but still leave a great deal to the ingenuity and experience of the paint manufacturer.

As another example one may refer to enamels which are used on transport, kerbside pumps, and so on. Experience over a number of years has shown that the alkyd type of enamel gives the best results from the point of view of length of service and good appearance. It is necessary, in order to obtain these good qualities, that the enamel should contain a certain minimum percentage of the alkyd resin, and this percentage is therefore specified and indicates the type of enamel which is required. The normal grades of alkyd enamel marketed by most reputable suppliers meet the specification which is laid down.

In the case of paints used on drums it is necessary to specify the physical properties which are required; for instance, resistance to petroleum products, drying time, degree of gloss, and resistance to the weather. There are many types of paint vehicle which provide satisfactory drum paints, and therefore it is not necessary to lay down a definite formulation.

In general, paint specifications should be based on first class types of paint which have been found satisfactory in service, and must be kept up-to-date and altered when necessary so that full advantage may be taken of new grades or types of paint which show superior properties. Another requirement is that the specifications must be applicable to the production of all countries which have a paint industry, as it is necessary in many overseas areas to purchase paint from local suppliers. It has been found that good specifications can actually raise the quality of paint in a country where the industry is in comparative infancy. The satisfactory results which are obtained from the use of good quality paints lead to demands for the same quality from other paint users, and this tendency raises the general quality of paints in the particular area.

To ensure that specification requirements are met it is necessary to have a certain amount of laboratory control over the consignments which are purchased. A very limited amount of chemical testing is necessary, and the main control is by physical tests. It is desirable that this work be carried out by people with some knowledge of paint manufacture and a good sense of proportion. The testing should include such determinations as drying time, opacity, resistance to petroleum products (if necessary), elasticity, and general properties such as gloss and fineness of grinding. It is preferable to depend on simple common-sense methods rather than on the use of complicated apparatus. As an example, the drying time of a paint can be determined simply and effectively by touching or pressing the film with the fingers and thumb; by this means it is possible to determine different states of dryness such as "surface dry," "hard to the touch," or "hard dry," and the results generally are more reliable than those obtained with special apparatus devised for a similar purpose. Naturally a certain amount of special apparatus is necessary, but all the tests should be as close to reality as possible.

The testing of the weather resistance of a paint is preferably carried out under the conditions in which the material is to be used. The chief agent in causing the natural breakdown of a paint film is undoubtedly strong sunlight, and this is assisted by the action of rain. The effect of solar radiation is so important that it is frequently found there is no comparison between the life of a paint film when exposed in a temperate climate to that of a similar film exposed in the tropics. Artificial weatherometers, employing an electric arc with a water spray and other means of ageing, have limited uses, as it is found to be very difficult to correlate the results obtained with the phenomena of natural weathering. Weatherometers undoubtedly have their place in the paint industry, but are not of much help in the type of testing under consideration.

Preparation of Surfaces for Painting

A large proportion of the paint used in the petroleum industry is applied to steelwork in the form of storage tanks, buildings, refinery plant, tank lorries, kerbside pumps, drums, etc. In most refineries and storage installations the steelwork is not exposed to severe chemical corrosive influences, such as are found in the gas industry or in many chemical plants. Most of the external corrosion of structures is caused by salt-bearing winds, since storage installations and refineries are generally located near the sea.

As indicated before, it is essential that steel surfaces should be thoroughly clean and dry when paint is applied. If paint is applied over moisture, particularly if traces of salt are present, breakdown of the film due to under-rusting is very rapid.

Another cause of paint failure is application over millscale, and for satisfactory results it is necessary that this be removed completely. The old method of de-scaling storage tanks was to expose them to the weather without painting, for periods up to two years, after which most of the scale would become detached

if conditions were at least slightly corrosive, and the surface would then be covered with a thick layer of rust. De-scaling by this means was a very uncertain procedure, since under dry conditions or with clean air the removal of the scale would be very slow, and under some conditions it might remain indefinitely. Even when the scale became completely detached, the film of rust contained moisture and salt, which were not effectively removed by scraping and wire brushing, and usually led to early breakdown of the paint film.

In the U.S.A. and some other countries it is common practice to remove millscale and rust by sand blasting storage tanks after erection. This method is effective, but needs very careful supervision to ensure complete removal of scale. The process is somewhat slow, and in Britain is generally very expensive.

It is considered that the best method of removing scale and rust from tanks and other vessels which are to be painted is to pickle the plates and structural members at manufacturer's works. The pickling method, which was developed by the Shell Group nearly twenty years ago, consists of removing the scale and rust by immersion in hot dilute sulphuric acid, washing in warm water, and finally immersion in a 2 per cent phosphoric acid solution which is maintained at a temperature of approximately 90° C. This process avoids neutralization of acid residues, and provides a surface which has very good adhesion for paint. Immediately the plates are dry after removal from the final bath and, whilst they are still warm, the first coat of priming paint is applied. By this means it is ensured that the surface has not become contaminated before the paint is applied, and the film therefore has first class adhesion. This process has been widely adopted in the petroleum industry, particularly for storage tanks, and its use has been extended to other industries. The cost is not prohibitive, and is recoverable in the reduction of maintenance during the whole life of the storage tanks and the avoidance of serious corrosion due to millscale.

Regarding the chemical treatment of steel, claims are often made that millscale and heavy rust may be removed by derusting fluids, generally based on phosphoric acid, which are applied by brushing on the steel surface. Experience shows that such solutions are not effective in this respect, and at the best can only remove light superficial rust. For the removal of scale and heavy rust by chemical means, it is necessary to immerse the plate in the acid solution.

Storage of Paint

It was mentioned earlier that paint must be in good condition when applied, and by this it is meant that the paint should be of the correct consistency for application and the whole of the pigment should be completely suspended in the vehicle. It frequently happens that, on long storage, the pigment separates out as a layer on the bottom of the container, and this is particularly noticeable with priming paints containing red lead and with undercoats which carry a high percentage of pigment. If the paints are used without being made homogeneous by stirring they can be completely spoilt; for instance, a red lead primer which is deficient in pigment gives a thin, glossy film which is generally too soft for the application of other paints, is far too thin, and has very little anti-corrosive value. However carefully the paint may have been specified and tested, the resulting film may be quite valueless if the painter himself neglects to prepare the paint properly for application or if he makes unauthorized additions of thinners or oils.

The main reason for the deterioration of paint in storage is the purchasing of consignments which are too large for immediate purposes. It would be ideal for paint not to be stored any longer than three months, and six months should be regarded as the maximum. Naturally the aim is to buy paints with good storage properties, but it is never good practice to store paints for very long periods under tropical conditions.

General Use of Paint

It is not proposed to describe in detail the types of paint used for all different purposes in the petroleum industry but to give general ideas on the subject. In the painting of steel structures, such as storage tanks, the general principle should be that the priming paint protects the metal from corrosion, and the function of the finishing paint is to protect the priming paint from deterioration due to climatic conditions. As indicated before, new steel plates should be de-scaled and a coat of primer applied at manufacturers' works. On arrival at site this primer is normally in good condition, although it may have suffered a certain amount of mechanical damage, which is made good, and a second coat of priming paint applied. In general, one coat of paint cannot be regarded as being completely continuous, this applying equally to priming paints or finishing paints. After the second priming coat, two coats of finishing paint are applied, and the type which gives the best results is a weather-resisting aluminium paint.

In the course of time, the aluminium paint wears thin due to slow oxidation of the binder. When the finishing paint is becoming obviously thin re-painting should be carried out and, if there is no rusting, it is sufficient only to apply one, or possibly two, coats of the finishing, *i.e.* aluminium, paint. If the steel surfaces are properly prepared and the original coats correctly applied, it should never be necessary to renew the priming coats, and the re-painting required should only be periodical applications of the finishing paint. This ideal, of course, applies only if scale and rust have been completely removed, but it must not be assumed that it is impracticable. It is certainly attained if painting instructions are correctly followed.

The type of priming paint for steel which has been found to give the best protection against atmospheric

corrosion is one containing red lead as the main ingredient of the pigment. Possibly the best priming paint of all is a straight red lead paint containing approximately 80 per cent of pure red lead, but such a paint, however, has very poor storage properties, and it is only possible to use it if it can be applied within a short time after manufacture. Furthermore, straight red lead paint is slow in hardening, and therefore is not very satisfactory for shop application. The types of priming paints which are recommended are those containing about 50 per cent of red lead together with other pigments, such as red oxide or graphite which help to prevent hard settling. The medium used should be bodied linseed oil with a proportion of bodied wood oil.

As mentioned before, aluminium paint for steel structures should be of the very long oil type, and the length of service which is obtained with this paint is remarkable. During the second world war, a number of tanks in different parts of the world remained unpainted, and it was found that on the shells the paint coating was still in good condition after as long as ten to twelve years, the aluminium still giving reasonable protection to the primer. As an average, re-painting of the sides of storage tanks should not be necessary more often than every nine or ten years, and on the roofs, which are exposed to more direct sunlight, the normal period for re-painting is after four or five years.

There is evidence that the use of white paint on storage tanks instead of aluminium reduces the internal temperature, which would tend to reduce evaporation losses from volatile products. Other methods, such as insulation and the use of floating roofs, are normally used to achieve this end, but it is worth mentioning that the life of white paint, even when based on an alkyd vehicle, is generally about half that of aluminium paint, so that the additional cost incurred in re-painting must be taken into account. Furthermore, the reduced temperature is achieved only whilst the paint retains its whiteness, and if the film is allowed to weather so that the primer is exposed, the result would be worse than if aluminium had been used.

During the past decade a good deal of investigation has been made into the application of sprayed metal coatings, such as zinc or aluminium, on steelwork as an additional protection against atmospheric corrosion. This process is undoubtedly effective, particularly if paint is applied over the sprayed metal coating. It is felt, however, that for the conditions normally found in petroleum refineries and storage installations, adequate protection of steelwork can be achieved by means of paint alone, but it should again be emphasized that this is the case only if the metal is properly cleaned and the correct paints are applied.

The protection of the inside of main storage tanks does not normally present any serious problem when dealing with refined products. It is considered necessary to paint the underside of roofs and the structural members, and it is normal practice to use the same primer as that employed for external work. This primer may be protected with a coat of finishing paint, although that is not so essential, since the film is not exposed to sunlight.

Considerable corrosion may occur in tanks carrying sulphurous crude oils, and in this connexion oil paints are completely useless. There is evidence from the U.S.A. that polyvinyl resin paints are successful, providing an adequate film thickness is built up by the application of about six coats. It is expected that paints based on the new epoxide resins may be used for internal protection of tanks carrying corrosive crudes, since this type is extremely chemically resistant, and is unaffected by petroleum hydrocarbons.

As regards refinery plant and vessels which are not insulated, the painting procedure is the same as described for storage tanks. In some instances, such as on a doctor treating plant, spillage of chemicals may occur, and conventional paints are of no use. Paints based on coal tar pitch generally give reasonable protection, but their appearance is unsightly. Chlorinated rubber paints are fully resistant to alkaline or acid spillage, but break down badly at temperatures above about 80° C. Here again, the problem may be solved by the use of paints based on epoxide resins.

During the past few years, there has been a general tendency to improve the interior painting of buildings in which a large number of workers is employed, by using colours on walls and machines which aim at providing the best working conditions. These colours are pastel shades, such as cream, ivory, and pale green for the walls and underside of roofs, whilst machines may be painted in a restful green colour. The use of such colours avoids dinginess and sharp contrasts as occur when walls are painted with a black dado with whitewash above. These improved painting schemes may be effected by the use of oil bound distempers on the walls and roofs and normal enamels on machines and plant so that no great extra cost is involved.

As regards pipelines, it is good practice to paint overground lines with red lead-containing primer and aluminium, but for buried lines paint is quite ineffective, and it is necessary to use heavy coatings based on bitumen or coal tar pitch.

Painting of Distributing Facilities

Painting of distributing facilities, such as tank lorries and kerbside pumps, does not call for much comment. Undoubtedly the best enamels available for this class of work are the alkyd type, which retain gloss for a number of years under temperate conditions, and for two or three years even when exposed to tropical sunlight. These enamels are more economical in use than nitro-cellulose lacquers, and do not require polishing to maintain good appearance.

Painting of Drums

Reference is made to the painting of drums, since a very large amount of paint is used for this purpose.

Until recently it has been the practice in many industries which market products in steel drums to use the cheapest type of paint, based on rosin, for external painting. Such paint retains its gloss and good appearance for one or two weeks, but after that time, if exposed to the weather, it becomes dull and cracks, and gives very little protection from rusting. The only advantage of this type of paint, apart from its cheapness, is that it is very quick drying. It is considered to be good practice to use drum paints of reasonably good quality which will retain a good appearance for three to six months, and which are, of course, resistant to spillage of the product. Generally the drying period for such paint is of the order of four hours, which is possibly rather too long for convenient operation. Nowadays air-drying drum paints based on synthetic resins are being produced, which dry in about a quarter of an hour and, unlike the rosin paints, have good weather resistance and are unaffected by spillage of petroleum products.

Lubricants drums are required to have a first-class appearance, and it should be normal practice for these to be painted by the manufacturer with a good stoving alkyd or other high quality synthetic enamel.

With heavy steel returnable drums it is necessary to avoid internal rusting which would cause contamination of the products carried. This problem was formerly overcome by a fairly general use of galvanized drums, but such drums are not entirely suitable for all products, and the solution adopted has been to line plain steel drums with a suitable lacquer. A number of types of lacquer have been tried for this purpose, but the most suitable to date has been the stoving phenolic resin type, which is applied by spray during the manufacture of the drum and is cured by heating at 200° C for half an hour. This lacquer coating has given satisfactory service for as long as five years, and there does appear to be a good case for using lacquer-lined drums in certain circumstances. Further trials are in hand with other types of resin.

Painting of Craft

The special problems which arise in the painting of craft could well form the subject of a separate paper.

The most troublesome matter in connexion with tankers is the corrosion which occurs on the inside of tanks carrying gasoline and other white products. This corrosion is so heavy that it may determine the life of a tanker. Naturally many trials have been made to find suitable paints for the interior of ships' tanks, the properties required being complete resistance to petroleum products, salt water, cleaning media, and steam, as well as good elasticity and adhesion. Promising results have been obtained in trials in the U.S.A. with polyvinyl based paints, whilst there is hope, from early tests, that paints based on epoxide resin may prove to be an answer to the problem.

Considerable progress has been made in recent years in painting the hulls of ships and, for ocean-going tankers, this can hardly be said nowadays to give rise to a corrosion problem.

DISCUSSION

J. R. Baddiley: In replying to Dr Footner's most interesting paper, I can not speak as a specialist in paint—but can only offer a few of the views of a group of people responsible for the paint work in an oil refinery. I am therefore limiting my comments to one or two of what seem to me to be the main points of the paper.

The first point is one which Dr Footner did not stress tonight, but he does mention it in his paper. He refers to the employment by petroleum companies of paint specialists. We believe that owing to the considerable bills for paint every year, that almost every major oil company, or major oil installation, should be able to justify the employment on site of an expert on paints. I would support that statement with two points. One is that to evaluate and compare the various paints for, say, a particular service, it would appear to be essential to keep complete and detailed records of all the circumstances relating to the application of the paint, and I do not think that normal painting forces are particularly interested in keeping such records. Again, to my knowledge, paint manufacturers are somewhat reluctant to divulge the actual contents of their products, and it seems to me that it is essential to have a grounding in paint technology to be able to talk with the manufacturers on an equal footing; and it is only with specialists following paints closely in the field, that it is possible to develop satisfactory specifications to meet all requirements. When Dr Footner discussed the preparation of surfaces for painting, we felt that he was dealing with the most difficult part of the whole subject, in that not even the best of paints will adhere to an insufficiently prepared surface. Pickling is obviously the ideal method of cleaning new plate work, etc., but I would query the statement that the initial primers, in these circumstances, last indefinitely. I would ask Dr Footner if it is a fact which has been proved to be the general case in practice.

Pickling, of course, is for new construction, but surely by far the greatest percentage of paint used is not for new work but for recoating old equipment. In these circumstances, obviously we have to go to other methods for preparing surfaces. As Dr Footner says, sandblasting is a very costly business, and I think it is also a very slow one. It is used frequently for small items of equipment which can be dealt with satisfactorily, but when one comes to the larger and more involved plants, then it seems to be out of the question, not only on cost, but because in many cases, the plants are not available for sufficiently long periods of time. On derusting preparations, we can, I think, only agree with Dr Footner. I believe that some paint manufacturers are adding phosphoric acid to their primers, but I do not believe that, once again, this is not entirely satisfactory. Leaving aside pickling and sandblasting, we would appear to be down to treating metals by using solvents for degreasing, and wire-brushing for removing loose scale and rust. To my mind, this is about the only quick method of preparing surfaces and probably the only method of tackling such things as pipelines on jetties, which in many cases are extremely difficult to service. All of this leads us to believe that, at the present moment, we are at something of a stalemate, in that all paints require perfectly clean surfaces, and to get all surfaces perfectly clean is not a practicable proposition.

I would like to support Dr Footner on the question of

spraying metal coatings. My attention has been drawn to cases where sprayed metal coatings have given excellent service in places where paint had previously failed. I wonder if, in view of the very careful surface preparation used for metal spraying, the paints used in these locations were applied with the same care.

Before finishing, I would like to refer to two experiences. During the large expansion of a refinery, the contractor checked and kept a careful note of the various manufacturers' paints used around the tanks and pipelines. After a period of operation, these paints were inspected, and it seemed to us to prove pretty conclusively that the normal lead primer was about the best for general service. At the same time, the red lead primers by no means agreed with one another on the service given. I wonder if this does not come back to the question of employing a specialist on the job, in that although records were kept of the way the paints were used, no record was kept of such things as the weather during application, which, I believe, can radically affect the life of one paint against that of another. Finally, on high temperature paints, our experiences with both aluminium type high temperature paints and silicon base paints have been good. Up to about 500° C we do find rust forming beneath the surface, and finally it has to be taken off and renewed. At higher temperatures, around 800° C, we find that the paint gives excellent service, but discolours, and we are compelled to paint for appearances alone. We find that when it comes to repainting, it is almost impossible to remove the initial paint, yet the following coats of paint will not adhere to the original. To date, we ourselves know of only one paint which will adhere to previously applied high temperature paint, but this is very expensive.

Dr Footner has drawn our attention to a subject which is not given the attention it requires.

Dr Footner: A few points have been raised on which I would like to comment. Firstly, to have paint specialists in every refinery or installation is certainly an ideal to be aimed at; possibly our method has been to centralize the business rather than to have the specialists all over the place. Naturally a man understanding paint and its application must be available at all installations, since so much depends on paint being in a usable condition and on its being applied properly. Whether every centre can justify a paint technologist who can speak intelligently to manufacturers is another matter, but it would be refreshing for the manufacturers, I think, to find such people.

The question was raised as to whether a primer really lasts indefinitely, shall we say, on a pickled surface. My experience is that an indefinitely long life is possible. A primer on a pickled or sand-blasted surface, if properly applied and protected by receiving the finishing paint when necessary, stays put indefinitely. Probably most people do not get that impression, because there is so much steelwork which has not been pickled or sand-blasted, and under those conditions it is not so easy to avoid under-rusting, but there is no reason why the primer should not last indefinitely, if protected by finishing coats and applied to a clean surface.

On the question of repainting existing equipment, there again it is largely a matter of supervision and painting quickly enough. I have known instances where repainting has been postponed for one or two years, on grounds of economy, and then it was not a matter of simple repainting, but of scraping down to bare metal and putting on four coats instead of one.

Sandblasting is, of course, expensive and dirty, as I said, and fairly slow. One man working one nozzle should be able to do 80 to 100 sq. ft. per hour, but it is not easy to attain this if the surface is very corroded.

The type of primer containing phosphoric acid is "self-etching" and based on polyvinyl resins, zinc chromate, and the phosphoric acid, which is normally mixed in just before use. There is some etching of the surface, and a thin anticorrosive film is obtained. This type of primer, in my view, hardly enters into the maintenance painting of steelwork in the petroleum industry.

The painting of jetty pipelines is mentioned as one of those almost impossible jobs, which, of course, it is. It depends once again how well the maintenance has been carried out, and whether the painting was done as quickly as it should have been. The difficulty is to make sure that the pipelines are dry, and that there are not salt deposits, which will ruin any paint system. Regarding variations in performance in different red leads, one could well get different results if the paints were applied on different days and under varying conditions. There is also the possibility, perhaps remote, that the paints were not all of the same quality, some may have been adulterated, some may have contained 100 per cent red lead. As regards heat resisting paints, there is one type of paint with which we have had considerable success on stacks which are subject to temperatures of the order of, say, 200° to 250° C and that is one containing a high percentage of a mixture of zinc dust and graphite, and a small amount of linseed oil binder. The theory is, roughly, that the binder is more or less volatized or decomposed in the course of time by the heat of the stack and leaves behind it a layer of zinc, which attaches itself to the metal. Applied properly, that paint, I think, is by far the best type of stack paint. Our general experience with aluminium heat resisting paints is that they just do not stand up to the weather. They are often very good as heat resisting paints, but not where weather resistance is required as well.

S. Barron: Dr Footner said that he had a very strong preference for red lead paints as primers on steel surfaces. Recently there has been a growing belief in the efficacy of zinc-rich paints for this purpose, and they are becoming very popular. What has been Dr Footner's experience with these zinc-rich paints?

Dr Footner: Zinc-rich paints have largely been on a trial basis, and I think probably their use would be justified if red lead paints did not do the work efficiently. The main objection to the use of zinc-rich paints is the high cost.

K. R. Garrett: We have carried out some experiments, using zinc-rich and red lead primers, and have found that one of the advantages of the zinc-rich type is that it is not necessary to remove the rust film completely before treatment, as one must do for other types of primer. All scale must, of course, be taken off. One does save a certain amount of money which can be offset against the higher price of the material.

Are we to understand from Dr Footner's address that red lead primers are better than those of zinc chromate? Quite a number of experiments were carried out by the U.S. Navy, and their results indicated that zinc chromate primers were preferable to certain red lead primers. Could he please give further details on this point?

I would like to ask Dr Footner for any further data he may have on the interior treatment of petrol tanks, because in many tanks water condenses and collects in the base and others are provided with a water seal. He has said that, except for the roofs, the insides of these tanks are not painted. I would suggest that the lower part of the tank is the most vulnerable point and might be painted.

I would also like to ask whether, after choosing an alkyd paint for general purposes, he would consider the use of a chlorinated rubber base type of air drying paint for outdoor exposure.

On the subject of applying four coats of paint in preference to metal spray, I heartily agree with this for large pieces of equipment such as bulk tanks, but for

smaller items I think that if one investigates the cost of metal spraying versus four coats of paint, it would be found that one coat of paint and metal spray would probably be cheaper, and, I suggest, better from a durability point of view.

Much aluminium paint is used on the outsides of storage tanks in refineries. Has Dr Footner any data on sparking from aluminium painted surfaces. There has been some work carried out recently on this subject.

If such a paint film breaks down and rust is formed, it is possible to strike the aluminium paint and rust together with a non-sparking tool and produce a spark.

Dr Footner: The last speaker raised a number of very interesting and possibly controversial points. First, the use of zinc-rich paint over rust. I know that is a point which is put forward in its favour, but I think a very dangerous point indeed. I do not subscribe to the use of any sort of paint on rust or moisture. There is one obvious advantage with zinc chromate primers, particularly in dealing with overseas installations where paint has to be imported, namely, that the keeping property of this primer in the container is better than that of red lead primers. Our experience indicates, however, that red lead-containing primers, provided they contain about 50 per cent red lead, are definitely better from the anti-corrosive point of view than the zinc chromate type. This fact has been shown by large-scale trials on storage tanks and, in seven marine atmospheres, the difference in favour of red lead primer is very marked.

In regard to the question of tank bottoms of refined product storage tanks. One aims nowadays, at eliminating water bottoms, but there is always a certain amount of water remaining, particularly with the type of tank bottom sloping away from the centre. I am of the opinion that it is difficult and uneconomical to use a paint on the bottoms of large storage tanks. It is quite a practical proposition in small storage tanks, or in tanks on airfields, if one uses the right paints, but it is not a proposition on the bottoms of main storage tanks. The way to prevent corrosion on those bottoms is to remove the millscale. Before we started pickling tanks we did get trouble with tank bottom corrosion, and it was undoubtedly due to electrolytic action set up between the steel and the large areas of millscale. There is a type of coating, one can hardly call it paint, which we use in refined products tanks, consisting of a mixture of cement and glue, in the proportions of ten of cement to one of glue, mixed into a slurry with water. It has the advantage that the plate does not have to be dry when the coating is applied, and it gives protection for up to two years. The cement wash maintains the water in the tank in an alkaline condition, and there is some evidence that it has a slowing up effect on sulphate-producing bacteria.

Regarding the comparison of chlorinated rubber paints with alkyd enamels, our experience is that the weather resistance of the alkyd enamels is far superior.

Regarding sparking from aluminium painted surfaces, published work shows that this can occur only if the film has been maintained at a temperature above 100° C for all types of aluminium paint except those based on a fine nitro-cellulose medium. In our standing painting instructions we lay it down that no heat resisting or any type of aluminium paint may be used on objects which are heated above 100° C, if they are in a dangerous atmospheric area. There is no evidence at all that aluminium paint used on buildings, storage tanks, rail-cars, and so on, is likely to give rise to incendiary sparks.

J. E. Winscombe: I feel sure that all members and guests appreciate the able manner in which Dr Footner has dealt with a subject which is important not only to the very extended interests of the petroleum industry but also to the manifold allied industries at home and abroad.

I am impressed with the indication that it is desirable to use paint stocks within nine months of manufacture, but I feel that in general a purchaser could not identify how long paint consignments may have been held at the supplier's premises before despatch. This feature, when considered with transit and other conditions, is likely on the whole to mean a very much longer period than nine months before average consignments of paint are available to the majority of users.

Might the audience have the benefit of expert advice upon the risk attributable to the use of aluminium paint. Instances of fire have occurred where aluminium powder and oily rags have been in contact under certain temperature conditions, and warnings in this respect have included the desirability of using non-ferrous tools when handling containers of aluminium powder.

In some circumstances steel coated with aluminium paint will emit sparks when struck with a metal striker, and such sparks may ignite mixtures of inflammable gases or vapour in the air. It is understood that these sparks are due to the thermite reaction between iron oxide and aluminium, and in this connexion the Department of Scientific and Industrial Research Committee (1953) are investigating paints available on the market which may safely be used in certain situations where combustible gases and vapours may exist.

The importance of this subject is emphasized by the recent decision of a committee covering the interests of the liquid fuel gas industry to recommend that cylinders (containers) of liquid fuel gas should not be treated with aluminium paint, hence it was considered that there was a general desire for some authentic guidance in the application of aluminium paint.

Dr Footner: Regarding the painting of liquid gas containers, it should be noted that in the U.S.A. all containers for propane, butane, or mixtures of those two are painted aluminium. There have been fires in liquid gas installations in the U.S.A., and possibly some of them have been unexplained. The type of paint used on those cylinders in repainting must dry very quickly, and for that reason it has usually been a nitro-cellulose type. It was to eliminate the danger of that type being used, that we, in our operations, have prohibited the use of aluminium on propane cylinders. Possibly the risk was negligible, but we thought that there was nothing in particular to be gained by having aluminium paint on the cylinders, and there was this faint possibility of sparking.

The other point raised was the fire hazard from aluminium powder. Under the right conditions finely divided aluminium in the presence of air may give rise to an explosion hazard, but this is an unlikely contingency with the grade used for aluminium paints. Nowadays, in possibly 95 per cent of aluminium paints, one does not use the dry powder, but a paste made up of two parts of powder to one part of white spirit, in which there would be absolutely no danger of spontaneous combustion.

R. L. Frost: I speak as a member of a paint manufacturing firm. Having heard what Dr Footner has said, I feel able to get on my feet without blushing. I personally found it a most interesting lecture, and I am sure that other members of paint manufacturing firms who are here will agree with me that Dr Footner shows a very keen appreciation of the necessity of giving the paint a chance to do what it is trying to do. I am sure that when other people in the paint trade who are not here read the lecture they will thank you, Dr Footner, for putting that aspect of the matter so clearly.

I should like to ask a question in connexion with the preparation in the U.K. of material which is going to be used, say, in a more tropical region: first, whether you have any information regarding the allowance to be made for the drop in viscosity which will presumably occur when materials made in the U.K. are stored and

used in more tropical regions. Secondly, whether the conditions under which drying tests are carried out in the U.K. are adjusted to simulate the conditions under which the paint will be used.

Dr Footner: Regarding the viscosity question, we do lay down viscosity limits, but our general experience has shown that it is not necessary to vary these limits for different climatic conditions. If the paint is a little thin when it arrives in the tropics, it may be an advantage, as it gives the painter no excuse for adding thinners or other materials.

Regarding drying tests, we do try to simulate tropical conditions. We were badly taken in some years ago with standard oil types of paint, which apparently dry quite well when tested in the U.K., but when used under fairly humid tropical conditions, lose their drying properties and remain sticky indefinitely, and following that bad experience, we now test all paints which are to be used in the tropics, at a temperature of 90° F and 90 per cent relative humidity.

W. L. Coates: Having listened to Dr Footner's most interesting paper, it seems to me that two points stand out most strongly; first, the wide variety of paint specifications to be considered, and, secondly, the meticulous care that must be given to preparation of the surfaces if satisfactory results are to be obtained—and even then there still remains an element of uncertainty. One is prompted to ask if in fact the real solution of this problem of protection has yet been found. The ideal paint would be one which I, or any other person not an expert on paints, could walk into a shop and buy and apply to the surfaces to be protected with a reasonable assurance of satisfactory results, without the necessity of going over every nook and cranny with a fine tooth comb to remove the last trace of rust or dirt which might impair the results.

It does seem surprising that the paint industry has not achieved more in this direction considering that it is one of the oldest industries or crafts in the world. Paint was probably one of the first things discovered by man, after fire, and probably even before he learnt to build a house, so that the industry has thousands, if not tens of thousands of years of experience behind it.

Take for comparison the motor car industry. Fifty years ago the proper handling of one of these vehicles was more or less the province of an engineer; today when one buys a car the manufacturer hands over something which a schoolgirl could drive and in the handling of which anyone with a modicum of common sense could hardly go wrong. The fact that that state of perfection can be achieved in half a century is certainly a challenging thought.

Admittedly the paint manufacturer will contend that good and lasting results can be obtained provided all the requirements are observed, such as the selection of the correct paint and adequate preparation of the surfaces. It is this very proviso, however, which is the nigger in the wood pile. Once rust sets in on a modern steel structure it is almost impossible to eliminate it, at least as an economical operation. One might almost say that it is there for all time, and certainly keeps breaking out again every few years. I should like to submit that while there is no doubt scope for research to improve the various properties of existing paints, particularly durability, the most urgent and most profitable direction in which research can be directed is towards finding some means for neutralizing, or inhibiting, the effect of rust—in short a paint which can be satisfactorily applied on top of a certain amount of rust at least. It does not necessarily follow that this must take the form of a pigment, it might conceivably be a chemical compound which would combine with the surface of the metal, even if the latter was in a rusty condition.

One final point. Many years ago the company with which I was associated had the roofs of their corrugated iron buildings painted with a black bituminous paint, which when first applied had a glossy finish. At the end of 12 months the surface had gone quite flat and some of the paint, in the form of a powder, could be removed by rubbing it with the fingers. At the end of three years most of the paint had disintegrated into powder and disappeared. Obviously the roofs could not be repainted with ordinary oil paint on top of the black bitumen, and to remove the latter entirely was also impossible. To meet the situation an aluminium bituminous paint was produced. This paint proved so satisfactory that when the remainder of a depot was being repainted after an interval of five years the roofs of the buildings could sometimes be left over until the next repainting. This paint does not appear to come into the favour which I should have thought, and I should be interested to know if Dr Footner has any observations to make on this point.

Dr Footner: Aluminium bitumin paint is certainly useful for bituminous coatings where oil paint can not be used. Its weather resistance, however, is inferior to that of oil-base aluminium paints. If aluminium bitumen paint gave a life of five or six years, then I would say, that ordinary aluminium paint, based on drying oils, would give a life of ten or twelve years. Another objection to aluminium bitumen paint for general use on refineries is that it is not oil or petrol resistant, as its binder is bitumen, which is immediately dissolved by contact with oil.

Regarding the suggested paint for all purposes which can be applied under all conditions, I should think, from the number of claims made, that there is a lot of research being done, and that a paint which can be applied over moisture and rust is invented every few months. But once again, the inventors are rather more optimistic than the users, and generally speaking, those claims are not substantiated. I feel that if such a paint were introduced, the specification for it would have to be highly meticulous.

Dr S. G. Burgess: I have enjoyed listening to Dr Footner's address and noticed that many precautionary measures that are required for painting in a refinery are applicable equally to painting in the London County Council's service.

The Council spends of the order of £2,000,000 per annum on painting, and almost every possible material that requires painting exists in the service.

In our experience the cost of painting is, on average, about four times the cost of the paint, varying from two to one for plain walls to about eight to one for sashes and about ten to one for bridges. This rough estimate, of course, includes the cost of preparation. I agree with the speaker that paints must be supplied ready for use and that every precaution should be taken that nothing is added to the paint. If unsuitable for use, it should be returned to the makers, because the addition of white spirit, linseed oil, or driers may seriously reduce the life of the dried film and may even gel the paint before application. Painters like to thin a heavily bodied paint, especially if a bonus system is in operation, and it is important that all solvents should remain in safe keeping in the painter's shop. I should like to ask Dr Footner if he has had any experience with lead cyanamide as a protective coating and also if he could give us any information on paints incorporating epikote resins. As regards the latter, the ease of application and the adhesion to a metal surface are of particular interest and also the drying time that should be allowed between coats to ensure that the previous layer is not softened and pulled up.

Dr Footner: We have done exposure tests on primers based on lead cyanamide, and the results look very promising, but for the present we are not using it on a large scale.

Regarding epikote paints, there are, of course, a number of formulations based on that type of resin, but I presume the speaker was referring to what is known as the "cold cure" type of paint. That type has remarkable resistance to chemicals, acids, alkalis, and so on, and it can be applied without difficulty, in two, three, or more coats, generally allowing an interval of six or eight hours or maybe overnight between the coats. This type of epikote paint hardens and cures at temperatures over 45° F. At lower temperatures the cure is held up, and results may be disappointing, but at the correct temperature, the paint becomes hard and resistant within a day or so, and becomes completely resistant to all types of chemicals and solvents and alkalis in about seven days.

F. M. Richardson: There are one or two points of details I would like to ask Dr Footner. First of all, I think he feels that a bad paint properly applied gives better results than a good paint indifferently applied, and I don't think this question of application and preparation can be overstressed. Can he confirm this?

He did mention on this question of long oil alkyds, glycerol esterification. I shall be interested to know if he supports the view that pentaerythritol esterified products, particularly under marine conditions, give much better results from the point of view of extreme durability.

He has mentioned the question of aluminium paints, but I gather that he refers to either a straight oil or an oleo-resinous type of material. Does he really mean that, or does he mean a long oil alkyd?

He mentions the question of paint storage, and a number of other speakers have referred to it. I think that the practice of most manufacturers is to date the drums in which they send out their products. Our complaint is that the storekeepers don't take any notice of the dates, and you can always find the oldest drums still waiting in the stores. I don't know whether his organization has any method of taking advantage of the habit of manufacturers dating drums.

Finally, a more general question, and a much more difficult one. It is the question of testing. You can have all the experimental equipment, corrosion chests, weatherometers, and everything like that, but there is only one way in my view in which to test paint, and that is to put it on and see how it stands. It is very difficult for a manufacturer to maintain test racks in more than a very limited number of fields. We have a marine rack, severe chemical corrosion, a London rack, a country rack, and so on, but four or five racks is as much as the average manufacturer can maintain, and I think I speak for the industry's interest in research, in saying what we would all like is some association with a company taking an intelligent interest in paint, who would, as these experimental paints came along, put them on test, preferably using them themselves, because we should then get the results employing the user's painting technique. If we prepare the panels and send them out, we take pains to get them just right, so I don't think it is a fair test. I do think there must be many paint manufacturers who would welcome the opportunity of getting their stuff tested—not when it has gone through the development stage, but in the early stages, when it is purely a chemist's problem and has not yet become sales material.

Dr Footner: Regarding your first point that application is more important than good quality paint, it depends on how bad that quality is. There are some paints which would never succeed even under the best conditions.

Regarding alkyds, we certainly agree that pentaerythritol esterified alkyds are good, and in fact we are using them, and they are covered in our specification. The aluminium paint we use is not a long oil alkyd type, and the best results are obtained, I think, with a 100 per cent oil aluminium paint or an oleo-resinous type containing at least 80 per cent of oil.

Regarding trials, I fully agree that any trials made by users should be with the actual paint, applied by themselves under their normal conditions.

Van der Hoeven: What are the possibilities of flame cleaning as a surface preparation in the petroleum industry?

Dr Footner: Flame cleaning has not been much used in the petroleum industry because of the fire hazard in "danger" areas. It is much more effective than scraping or wire brushing for surface preparation, but not as effective as pickling or sandblasting in removing every trace of scale. Where the two latter processes are not feasible, flame cleaning is easily the best alternative. In the industry it is being used on the hulls of ships, and I think, that on the topsides, above water level, it is proving very practicable as a means of surface preparation.

W. J. Brooker: I would like to speak for the painting contractor and join issue with Dr Footner and our friend who said, I believe, that he came from the L.C.C. Dr Footner said in the early part of his address, in emphasizing the importance which should be attached to painting, that on the question of cost it was found that labour exceeded the cost of materials by four times. Now this gives a quite wrong impression. I will not presume to give a lesson in estimating to those present, but I will give you an example which refutes the question of four times.

We painting contractors cannot control the price of paint, and, taking materials first, if you use a red lead paint, which, at 50*s* per gal, would not by any means be equal to Type 1 or 2, and you add 10 per cent for profit, giving a selling price of 55*s* per gal, and you now divide by a coverage rate of 60 (which is being generous), you will get a figure of around 11*d* to 1*s* per yard super. Now take aluminium paint at 30*s* per gal, again not by any means the best quality, add 10 per cent and take a coverage of 70 yards per gal, you get a price around 6*d* per yard super. With two coats of aluminium and a coat of red lead primer we now have 2*s* for material.

If you will allow the average painting contractor a selling price per painter hour of 6*s* bearing in mind that he pays 3*s* 8*d* per hour, plus travelling time, plus holidays with pay, plus fares, plus Employers Insurance Contributions, together with other overhead charges and some profit, it is not an unreasonable figure to estimate upon. The application of red lead is by brush at, say, an average of 7 yards per hour, on tankage, allow him 7 yards per hour for the first coat of aluminium by brush, and while it is good practice to spray the second coat of aluminium, let us take this also at brushing rates, *viz.* 7 yards per hour. We get 72 pence divided by 7 and multiplied by 3, and this equals 2*s* 7*d* for labour, which leaves a substantial margin for the preparatory work in cleaning, etc., before labour is four times the cost of materials.

Now a manufacturer has talked about giving the paint a chance, and I agree with him; but the painting contractor, in trying to give the paint a chance, has to allow for inclement weather, and if he did this on all occasions, he would just price himself out of business.

I would suggest to all oil companies that they become more selective, and not continue to chase the bottom

prices. It is no use sitting on the specification during the best months of summer, passing it out to the contractor with about ten days to prepare an estimate, and having the work started in September. They can get into touch with the National Federation of Master Painters, whose headquarters are in Manchester, and they would give them the names of half a dozen contractors in any part of the U.K. who will guarantee good workmanship. The oil companies, however, are no different from property owners, who will always accept the lowest tender.

Dr Footner: On your remarks about drawing up the specifications during the summer and painting during the winter, I have come across it, but I think perhaps that sort of thing is on its way out, and that the oil companies are doing their best to reverse things and think about specifications during the winter.

I do not want to go into details about the cost of painting, but I certainly did not intend to cast any aspersions on painting contractors.

F. F. Nye: Dr Footner mentions the use of paints on stacks and things up to a temperature of approximately 200° C. Has he had any further experience of their usage at temperatures above that? I was thinking of ones with considerably higher temperatures, as on a cat cracker regenerator stack, where you can get a very high temperature. Is there a paint or anything that will stand up to conditions like that?

Dr Footner: I have had experience only with zinc dust graphite under those conditions, and this paint does give reasonable service up to over 300° C.

Dr E. B. Evans: Could I ask Dr Footner a rather elementary question? You referred to the effect of sunlight on the length of life of a paint film. Is that a quantity or quality effect? Does it depend merely on the intensity of the sunlight, or on the quality of the sunlight available in different parts of the world? It would be interesting to have a little further information on that point.

Dr Footner: I have no quantitative information, but my feeling is that it depends largely on the quality of the sunlight.

I. Cameron: I speak not as a paint expert but as a mere engineer, whose misfortune it was for some years prior to the war to have to look after the maintenance painting of a large refinery, and I should like to say in answer to Mr Brooker that we certainly did not do our outside painting in the winter. We did our indoor painting then, and our outdoor painting was done in the six summer months. Usually, we adopted the method of hand cleaning, *i.e.* chipping, scraping, and wire brushing, followed by a coat of red lead primer and two coats of finishing paint on general structural steel work and tanks, and by that means, with very careful Company supervision of the cleaning and application, particularly cleaning, we got a life of three to four years, and then we started all over again.

Referring to the effect of sunlight, we used to test this by exposing test plates to the rays of an ultra-violet lamp. We were fortunate to have on the staff a chemist who had spent a long time in the paint industry, and we found that with the assistance of his expert interpretation of the results obtained from the test plates, we got a very good indication of the likely life of a paint. The ultra-violet lamp used to show up crazing and chalking and things like that in quite a short time. Perhaps Dr Footner would let us have his views on this procedure.

There is another point which Dr Footner made on the pickling of tank plates in the shops and painting them before erection. I should like to ask what steps are taken on the site, after the plates are assembled in the tank and welded, to protect the plate at the edges where the paint film has been destroyed by the heat of welding and to make good the damage to the paint surface suffered in transport.

Dr Footner: You mentioned that with wire brushing, scraping, making good the paint, and so on, it was necessary to repaint every three or four years, but I think I can safely say that with the preparation of steel work by pickling or sandblasting, the time would certainly be nearer six or eight years, unless you were in an extremely exposed, ocean installation more or less surrounded by the sea. I don't know of any location in the U.K. where, if proper preparation is carried out, one needs to repaint more often than every five to seven years. That, of course, has arisen not only from good preparation, although that is the main factor, but also by the use of aluminium paint.

Regarding the picking out of bad paints by ultra-violet exposure, my comment there is that it would pick out the very, very worst only, the type of rosin paint to which I have referred once or twice, but among reasonably good paints, it is not likely to be selective. With regard to pickled plates and the margins of pickled plates, there are two ways of handling that problem—some companies prefer to paint the plates all over after pickling, but that gives the possible hazard of volatizing lead, and possibly affecting the health of the welders. The other method is to leave the margins unpainted, but to apply a rust preventive, of the oily type which, under reasonable conditions will prevent rusting for perhaps, four to six months. That film, of course, is burnt off by the welding and disappears easily. All margins should be painted as soon as possible after welding.

C. C. Quiney: My job is also concerned with the application of paint as opposed to its manufacture.

Dr Footner has mentioned at some length the "pickling" of tank plates and, in my experience, I feel that it is absolutely the ideal solution for the prevention of rusting and the ultimate life of the paint films. The thing I cannot understand, however, is that on every site I visit where the plates are erected, I find that something like 20 per cent, and probably more in some cases, of the surfaces have been so badly scored by being dragged on the ground, that the whole object of pickling seems to have been lost, and quite severe corrosion has already commenced.

I do not know what could be done to obviate this, but, as we are all seeking the ideal or best form of preparation before applying the various paint coatings, it does seem a pity that something cannot be done to prevent careless handling on site or in transit.

Dr Footner: I would say that 20 per cent is a very high average percentage of the paint coating damaged. The amount of damage depends on the handling during erection, and varies, of course, with the time the plates have lain in the manufacturer's yard or on site before they have been erected, but I think your view is slightly pessimistic. I have seen many tanks, which have been erected in South America and other places, on which I have been surprised to find that the damage to the paint is negligible. They have been big tanks with heavy plates, and it really becomes a mechanical problem.

Dr F. R. Himsworth: We have found exactly the same thing. Tank plates which had been phosphated and primed suffered very severe damage in handling and erection. The result was that before the tank could be erected and painted a good deal of rusting had taken place. This was probably more severe than it would

have been on other sites, since the atmosphere in a chemical factory is more corrosive than that in a refinery. But it is a very real disadvantage. One of the virtues of metallizing is that it stands up to rough treatment of this kind much better than any other surface treatment, and I think one could guarantee to erect metallized steel without damage of any kind. The question is entirely one of cost, and metallizing is justified if it gives sufficiently improved results. An earlier speaker complained that comparisons of painting with metallizing weren't fair, because the metallized specimens got better surface preparation. But if one made things equal by giving the painted steel the same preparation, that is by shot-blasting, the costs of the two would become practically equal, and if the costs are the same, then metallizing is the better system, because three- or four-thousandths of an inch of zinc is undoubtedly a better primer than red lead or any other paint type of primer.

Dr Footner: I agree with Dr Himsworth that under conditions of chemical pollution, metallizing probably is justified, although from reports I have had from different places, I believe there are cases of metallizing failing under such conditions. But I still feel that, for the normal exposure in refineries and installations, the extra cost of metallizing would not be justified, and of course, on the matter of surface preparation, it must be borne in mind that pickling is generally about one-third, or one-quarter, the price of sand or shot blasting.

Dr E. B. Evans: Well, gentlemen, I am afraid we shall have to draw this very interesting discussion to a close, but I would remind members and visitors that written contributions to the discussion will be very welcome, if they will send them along to the Editor.

We have listened tonight to a very interesting and informative paper from Dr Footner, on which he has drawn very widely from his experience, both in this country and abroad. I believe, in fact, that Dr Footner is off to India very soon, and while thanking him for delivering to us this very excellent paper, we will take the opportunity of wishing him a very successful trip.

Dr Footner's paper has, apart from its intrinsic merits, had the additional virtue of provoking a most interesting and stimulating discussion. I would like to thank him on your behalf, and also Mr Baddiley, who opened the discussion, and all the other gentlemen who have contributed to such an interesting evening's proceedings.

PREPARATION AND PHYSICAL PROPERTIES OF SULPHUR COMPOUNDS RELATED TO PETROLEUM

PART 3. SEMI-AROMATIC SULPHIDES*

By S. F. BIRCH, R. A. DEAN, and E. V. WHITEHEAD

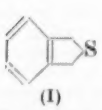
SUMMARY

The synthesis, characterization, and physical properties of four typical bicyclic monosulphides in a high state of purity is described, these compounds consist of an aromatic nucleus fused either to a five- or six-membered fully saturated sulphur-containing ring, and include 1- and 2-thiaindane, 1- and 2-thiatetralin. The reactions of these sulphides with several reagents are described.

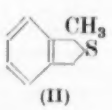
THE preparation and physical properties of a number of the simple monocyclic sulphides have been described in a previous part of this series.[1] The present paper gives an account of the extension of this investigation to the corresponding bicyclic derivatives in which a benzene ring is fused to a cyclic sulphide ring.

There is as yet no evidence for the presence of bicyclic sulphides of this type in straight-run petroleum distillates. Fully saturated bicyclic sulphides have, however, been isolated from acid sludge obtained in the treatment of Agha Jari kerosine extract.[2] Previously Brown and Meyerson,[3] from a mass spectrographic investigation of the sulphur bodies in a West Texas heater oil, had concluded that besides monocyclic, bi- and tri- cyclic sulphides were also present and were responsible for the objectionable odour, and Hoog [4] had shown the presence of bicyclic sulphides in a gas oil of Middle East origin by the examination of its desulphurization products. Although so far no aromatic bicyclic sulphides have been identified in straight-run petroleum naphthas, there is good reason for suspecting the presence of compounds of the benzothiophene type in the higher boiling fractions, *i.e.* of b.p. 210° C and upwards, of catalytically cracked naphthas.

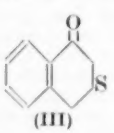
2-Thiaindane † (I) (*o*-xylylene sulphide) was first described by Leser [5] and later by Hjelt,[6] who obtained it by the action of potassium sulphide on *o*-xylylene dibromide. The yield by this method, but with



(I)



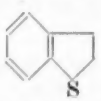
(II)



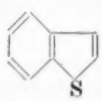
(III)

sodium sulphide, is, according to v. Braun, Bayer, and Kaiser,[7] 40 per cent. The corresponding 1-methyl-2-thiaindane (II) was also prepared by v. Braun and Weissbach [8] by this route in 70 per cent yield, and by the Clemmensen reduction of 4-keto-2-thiatetralin (III) in 30 per cent yield, a reaction involving the rearrangement of the thia*cyclo*hexane ring to the corresponding methylthia*cyclo*pentane structure. This rearrangement was subsequently confirmed by Leonard and Figueras.[9]

The isomeric 1-thiaindane (IV) (2 : 3-dihydrobenzothiophene) has been prepared by several workers. Fricke and Spilker [10] first obtained it in 17 per cent yield by the reduction of benzothiophene (thianaphthene) (V) with sodium in boiling alcohol.

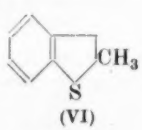


(IV)



(V)

v. Braun, Bayer, and Kaiser [7] and Challenger and Clapham [11] described its preparation from diazotized *o*-amino(2-chloroethyl)benzene with potassium xanthogenate. Bennett and Hafez [12] similarly obtained the sulphide from *o*-amino(2-hydroxyethyl)benzene. Bordwell and McKellin [13] isolated the sulphide in 92 per cent yield by reduction with lithium–aluminium hydride of the sulphone, which Truce and Milionis [14] prepared by cyclization of the ω-phenylalkanesulphonyl chloride.



(VI)

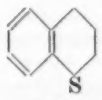
Hurd and Greengard [15] isolated what they considered to be 2-methyl-1-thiaindane (VI) from the rearrangement products of phenyl allyl sulphide.

1-Thiatetralin (VII) (thiochroman) was obtained in 80 to 85 per cent yield by v. Braun [16] from diazo-

* Paper received at the IP on 10 September 1953.

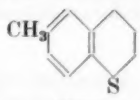
† There is at present no entirely satisfactory system of nomenclature for sulphur compounds. According to the system employed, o-xylylene sulphide can be termed : 2-thiaindane, thiophthalan, 3 : 4-benzothia*cyclo*pentane, 3 : 4-benzo-2,5-dihydrothiophene and 1 : 3-dihydro*iso*thianaphthene. For the simple compounds the system used is that adopted by the Advisory Committee of the API Research Project 48 on the recommendation of the Nomenclature Committee of the Division of Petroleum Chemistry. To avoid confusion, however, both the thia designation and the previously accepted names have been given.

tized *o*-amino(3-chloropropyl)benzene with potassium xanthogenate, and from thiochromanone by

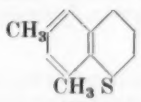


(VII)

Krollpfeiffer, Schultze, Schlumbohm, and Sommermeyer,[17] Cagniant and Delurzarche,[18] and Truce and Milionis.[14] Bordwell and McKellin [13] also prepared this sulphide by reduction with lithium–aluminium–



(VIII)

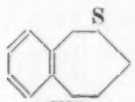


(IX)

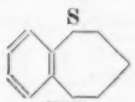
hydride of the sulphone which may be prepared by the method of Truce and Milionis.[14] 6-Methyl-1-thiatetralin (VIII) and 6 : 8-dimethyl-1-thiatetralin (IX) were prepared similarly by Krollpfeiffer *et al.*[17]

3 : 4-Benzo-1-thia*cyclo*heptane (*homoiso*thiochroman) (XII) was prepared by v. Braun, Bayer, and Kaiser [7] in 40 per cent yield by ring closure of the appropriate dibromide with sodium sulphide.

Cagniant and Delurzarche [18] and Truce and Milionis [14] starting from thiophenol synthesized 4-keto-2 : 3-benzo-1-thia*cyclo*heptane, which on reduction



(XII)



(XIII)

gave 2 : 3-benzo-1-thia*cyclo*heptane (*homo*thiochroman) (XIII).

The four sulphides described below were prepared on a sufficiently large scale to enable the intermediate and final materials to be effectively purified.

2-Thiaindane and 2-thiatetralin were obtained in good yield from the corresponding dibromides by ring closure with sodium sulphide. 1-Thiaindane was prepared from benzothiophene by reduction with sodium and alcohol using the method of Fɪicke and Spilker.[19] Although reaction conditions were varied to obtain an improved yield, it was not possible to increase this above 26 per cent. The availability of benzothiophene commercially, however, made this route attractive in spite of the poor yield. 1-Thiatetralin was obtained from thiophenol in 63 per cent yield by the method of Krollpfeiffer. The sulphides were purified through their mercuric chloride complexes which were recrystallized to constant melting point. The physical properties of the pure sulphides are given in Tables I and II. Infra-red and ultraviolet spectra were recorded on pure samples of each compound (Figs 1 to 8).

In their chemical properties marked differences were observed in the behaviour of the 1- and 2- thia- derivatives, but there was a close similarity between each of the two 1- and 2- substituted compounds. As would

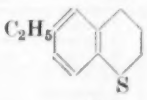
TABLE I

Physical Properties of the Aromatic Bicyclic Sulphides

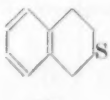
Sulphide	Boiling point *				d^{20}	d^{25}	Estimated purity, mol %	Estimated m.p/f.p. for zero impurity	Cryoscopic constant, mole % per ° C
	B.p. ° C at 760 mm Hg (extrapolated)	Antoine constants							
		A	B	C					
1-Thiaindane	235·58	7·0296	1780·8	193·62	1·1398	1·1358	99·80	−3·23	1·79
2-Thiaindane	241·5	7·0961	1843·5	195·87	—	1·1446	99·92 ± 0·02	+24·93 ± 0·01	1·52
1-Thiatetralin	254·0 (decomposition at 180° C approx)	8·158	2683	254·5	1·1249	1·1210	99·74	−14·91	1·38
2-Thiatetralin	264·7 (decomposition at 240° C approx)	7·1160	1933·2	191·76	1·1328	1·1289	99·63	+ 1·06	2·27

* The boiling points were determined using the Swietoslowski apparatus. Inter- and extra-polations were made using the calculated constants for each compound in the Antoine equation $\log_{10} P = A - B/(C + t)$, where A, B, and C are constants and P = pressure in mm Hg, and t = temperature in ° Celsius.

Cagniant and Delurzarche [18] obtained 6-ethyl-1-thiatetralin (X) by the condensation of 1-thiatetralin, prepared by Krollpfeiffer's method, with acetyl chloride followed by the Clemmensen reduction of the resulting ketone.



(X)



(XI)

2-Thiatetralin (*iso*thiochroman) (XI) has been prepared both by v. Braun and Zobel [19] and by Holliman and Mann,[20] with yields of 40 and 56 per cent, respectively. Although v. Braun and Weissbach [8] obtained 1-methyl-2-thiaindane by the Clemmensen reduction of 4-keto-2-thiatetralin, reduction of the corresponding hydroxy- or chlorothiatetralin gave 2-thiatetralin.

TABLE II

Refractive Indices of the Aromatic Bicyclic Sulphides

Sulphide	Refractive index at 20° C					Refractive index at 25° C				
	Hydrogen 6563	Sodium 5893	Mercury 5461	Hydrogen 4861	Mercury 4358	Hydrogen 6563	Sodium 5893	Mercury 5461	Hydrogen 4861	Mercury 4358
1-Thiaindane .	1·6126	1·6195	1·6255	1·6375	1·6532	1·6101	1·6170	1·6230	1·6349	1·6506
2-Thiaindane .	—	—	—	—	—	1·5983	1·6038	1·6086	1·6180	1·6298
1-Thiatetralin .	1·6082	1·6147	1·6204	1·6317	1·6463	1·6058	1·6122	1·6179	1·6292	1·6438
2-Thiatetralin .	1·6022	1·6077	1·6125	1·6219	1·6338	1·5999	1·6054	1·6102	1·6196	1·6313

Considerable difficulty was experienced in the accurate determination of these values, believed to be due to oxidation of the sulphide on the prism of the refractometer. Correlation of these values by Forziati's method [25] indicates that these results are accurate to $\pm 0{\cdot}0001$ of the values quoted.

be expected from their structure, the thiaindanes and thiatetralins combine the properties of the cyclic sulphides with those of substituted aromatic compounds. The behaviour with aqueous mercuric acetate solution of 1- and 2-thiaindanes and 2-thiatetralin has been described by Birch and McAllan.[21] The remaining sulphide, 1-thiatetralin, has now been shown to be practically unreactive, and to resemble 1-thiaindane in this respect. All four sulphides form normal derivatives of thioethers, including sulphoxides, sulphones, mercuric chloride complexes, and methiodides. They are far more reactive to atmospheric oxidation than the saturated cyclic sulphides, and this is particularly marked with the 2-thia- derivatives which is undoubtedly due to the $Ph–CH_2–S–$ structure in the molecule. It was found that unless air was rigorously excluded from specimens of these compounds they were partially converted to higher boiling compounds, from which the sulphoxide was obtained with 2-thiatetralin, and amorphous red and blue compounds with 2-thiaindane. Although the 1-thia compounds tended to give coloured products in the presence of air, the amount of high boiling material formed was very small and in no way comparable with the 2-thia derivatives.

The action of concentrated sulphuric acid varies

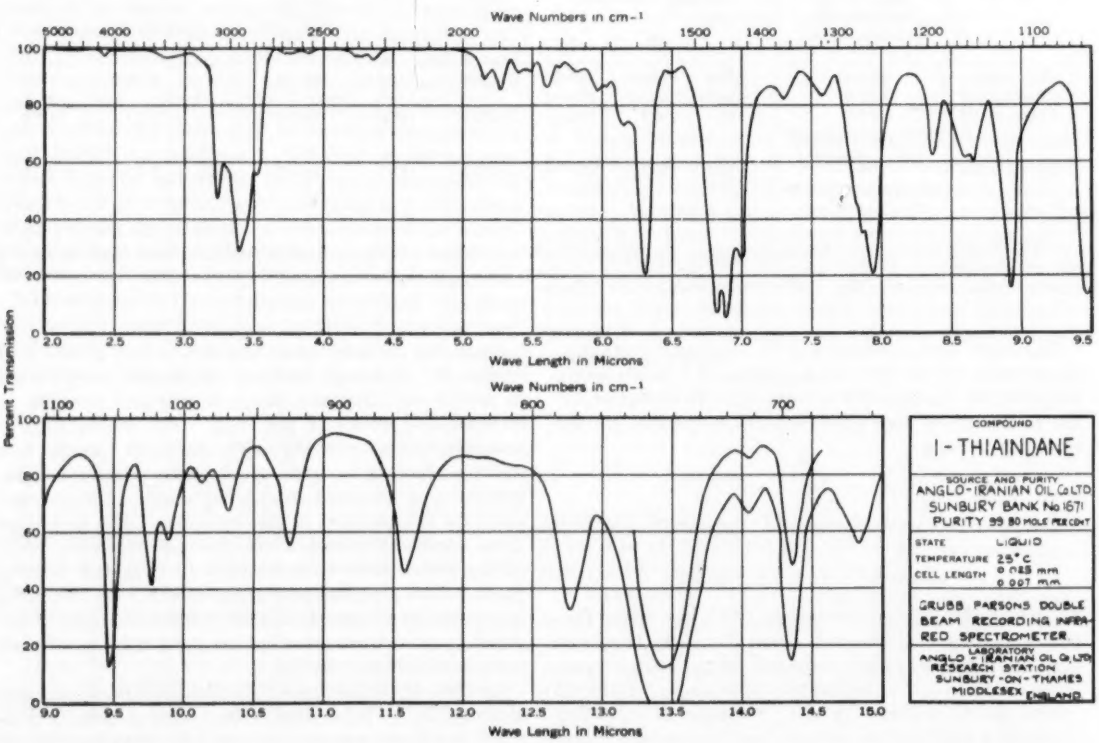


FIG 1

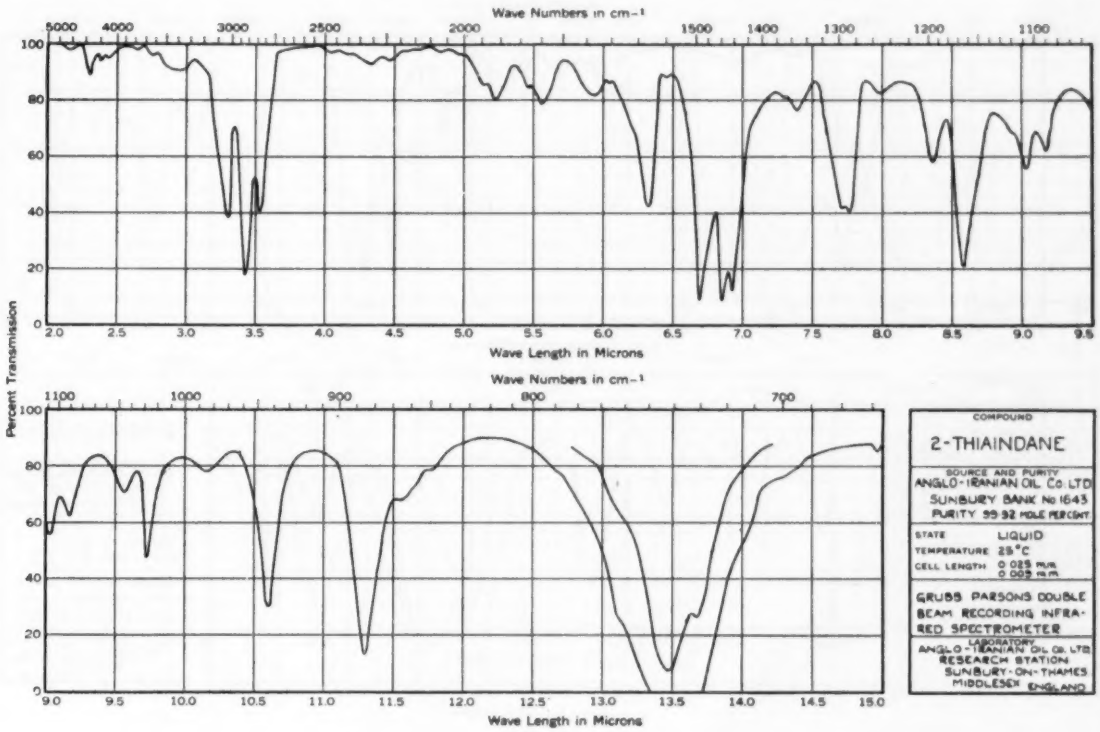

Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
Percent Transmission
Wave Length in Microns
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Numbers in cm⁻¹
1100 1000 900 800 700
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
COMPOUND
2-THIAINDANE
SOURCE AND PURITY
ANGLO-IRANIAN OIL CO. LTD.
SUNBURY BANK No 1643
PURITY 99·92 MOLE PERCENT
STATE LIQUID
TEMPERATURE 25°C
CELL LENGTH 0·025 m/m
0·005 m/m
GRUBB PARSONS DOUBLE BEAM RECORDING INFRA-RED SPECTROMETER
LABORATORY
ANGLO-IRANIAN OIL CO. LTD.
RESEARCH STATION
SUNBURY-ON-THAMES
MIDDLESEX ENGLAND

FIG 2

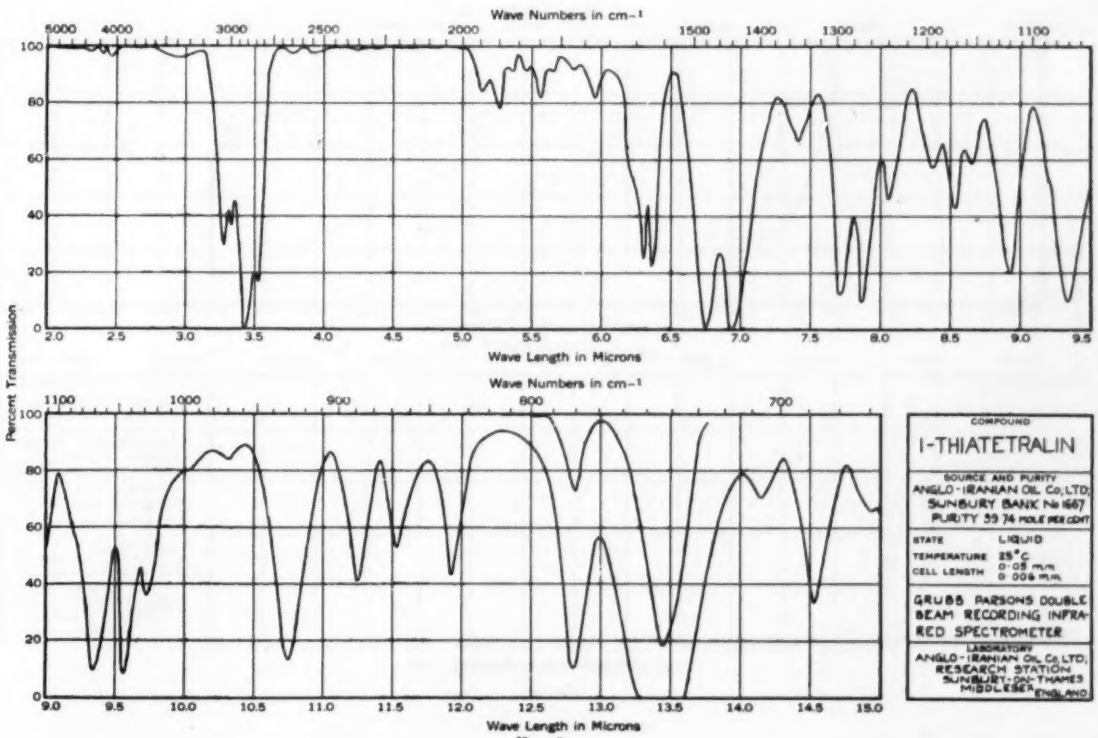

Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
Percent Transmission
Wave Length in Microns
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Numbers in cm⁻¹
1100 1000 900 800 700
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
COMPOUND
1-THIATETRALIN
SOURCE AND PURITY
ANGLO-IRANIAN OIL Co. LTD.
SUNBURY BANK No 1667
PURITY 99·74 MOLE PER CENT
STATE LIQUID
TEMPERATURE 25°C
CELL LENGTH 0·05 m/m
0·006 m/m
GRUBB PARSONS DOUBLE BEAM RECORDING INFRA-RED SPECTROMETER
LABORATORY
ANGLO-IRANIAN OIL Co. LTD.
RESEARCH STATION
SUNBURY-ON-THAMES
MIDDLESEX ENGLAND

FIG 3

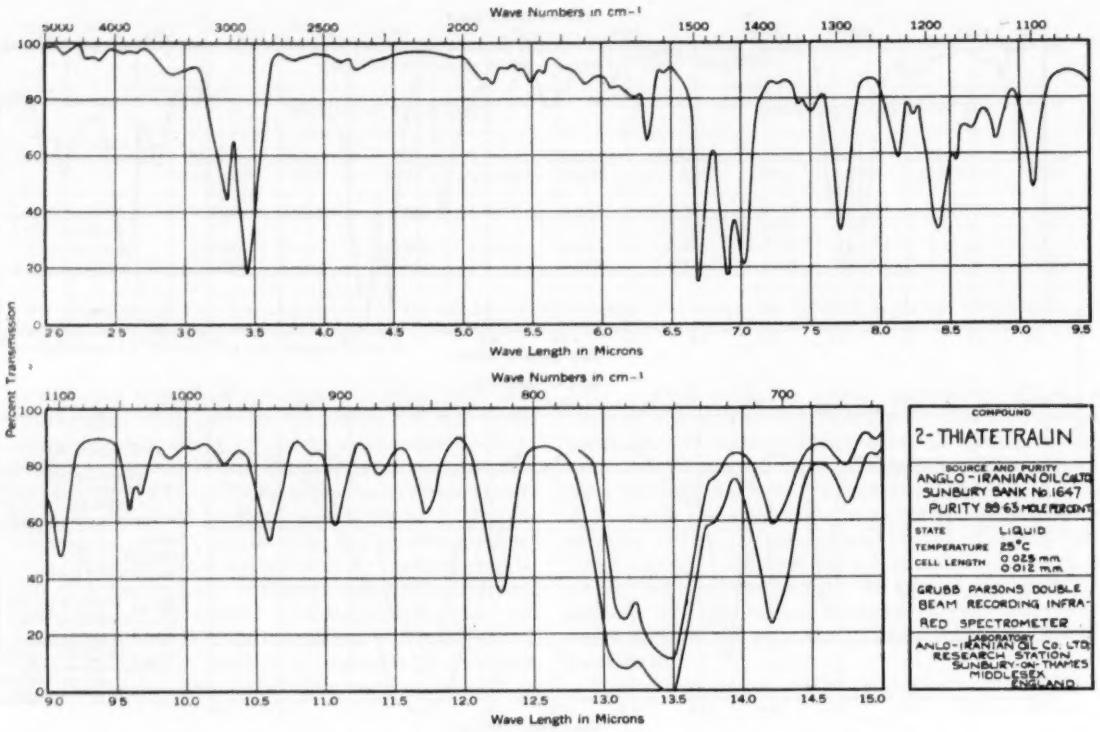

Wave Numbers in cm⁻¹
Percent Transmission
Wave Length in Microns
Wave Numbers in cm⁻¹
Wave Length in Microns
COMPOUND
2-THIATETRALIN
SOURCE AND PURITY
ANGLO-IRANIAN OIL CO LTD
SUNBURY BANK No 1647
PURITY 88·65 MOLE PERCENT
STATE LIQUID
TEMPERATURE 25°C
CELL LENGTH 0·025 mm
0·012 mm
GRUBB PARSONS DOUBLE BEAM RECORDING INFRA-RED SPECTROMETER
LABORATORY
ANGLO-IRANIAN OIL Co. LTD. RESEARCH STATION, SUNBURY-ON-THAMES MIDDLESEX ENGLAND

FIG 4

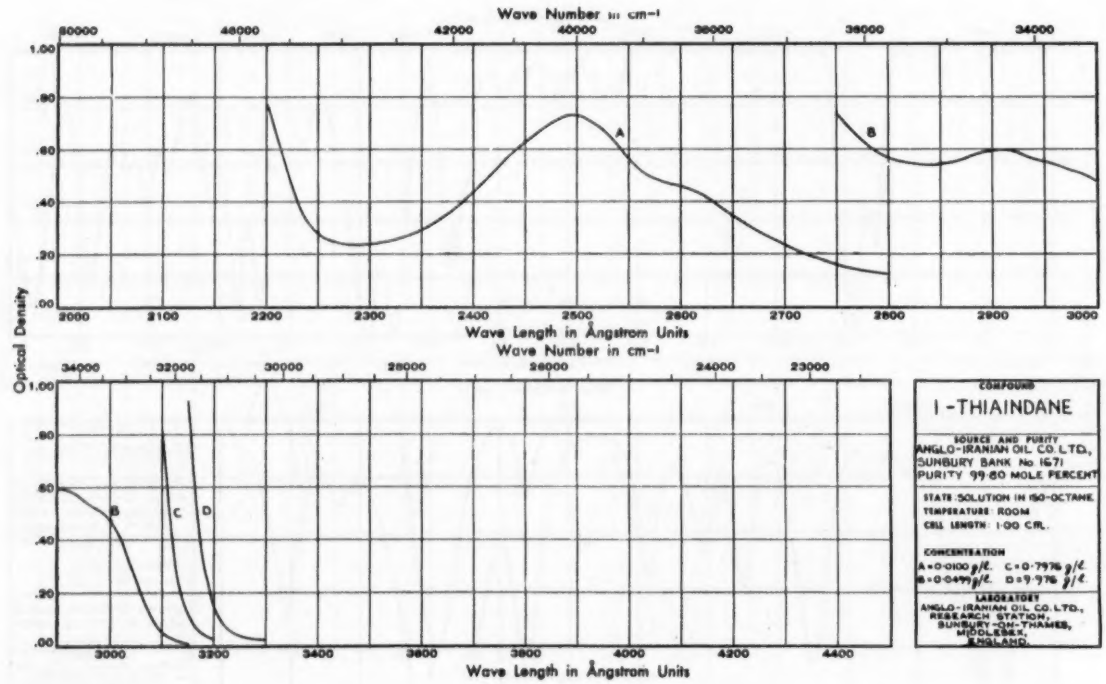

Wave Number in cm⁻¹
Optical Density
A
B
Wave Length in Ångstrom Units
Wave Number in cm⁻¹
B
C
D
Wave Length in Ångstrom Units
COMPOUND
1-THIAINDANE
SOURCE AND PURITY
ANGLO-IRANIAN OIL CO. LTD.,
SUNBURY BANK No 1671
PURITY 99·80 MOLE PERCENT
STATE SOLUTION IN ISO-OCTANE
TEMPERATURE ROOM
CELL LENGTH 1·00 C.M.
CONCENTRATION
A = 0·0100 g/c. C = 0·7976 g/c
B = 0·0499 g/c. D = 9·976 g/c
LABORATORY
ANGLO-IRANIAN OIL CO. LTD., RESEARCH STATION, SUNBURY-ON-THAMES, MIDDLESEX, ENGLAND.

FIG 5

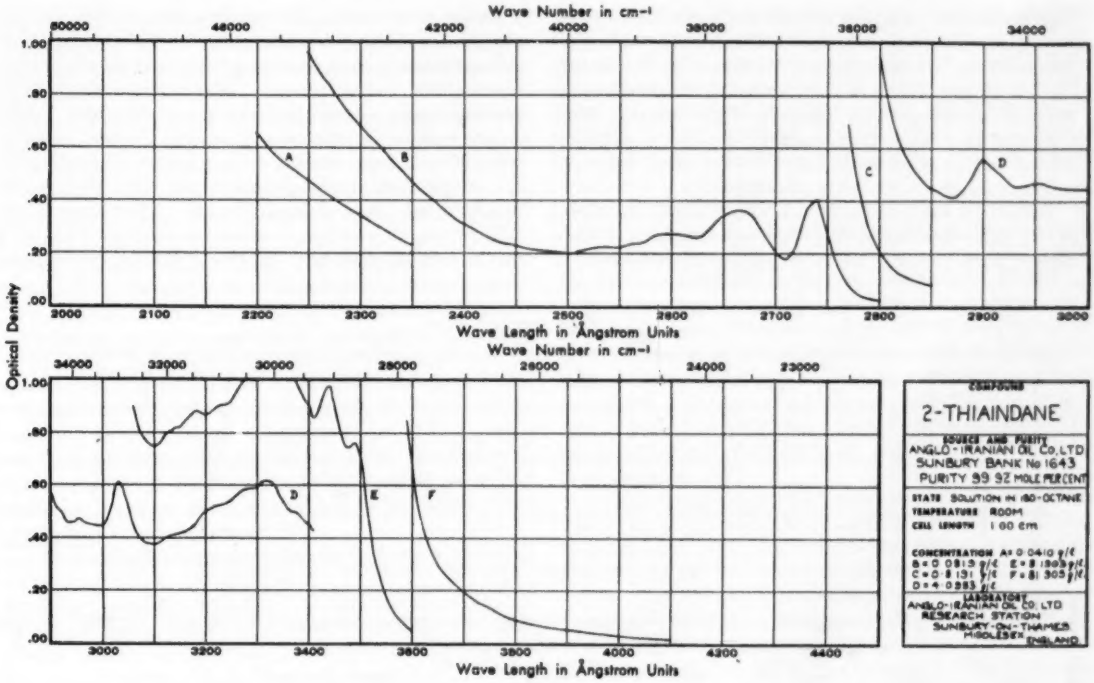

Wave Number in cm⁻¹
50000
46000
42000
40000
38000
36000
34000
1.00
.80
.60
.40
.20
.00
A
B
C
D
2000
2100
2200
2300
2400
2500
2600
2700
2800
2900
3000
Wave Length in Ångstrom Units
Optical Density
Wave Number in cm⁻¹
34000
32000
30000
28000
26000
24000
23000
D
E
F
3000
3200
3400
3600
3800
4000
4200
4400
Wave Length in Ångstrom Units
COMPOUND
2-THIAINDANE
SOURCE AND PURITY
ANGLO-IRANIAN OIL Co. LTD
SUNBURY BANK No 1643
PURITY 99 92 MOLE PERCENT
STATE SOLUTION IN ISO-OCTANE
TEMPERATURE ROOM
CELL LENGTH 1·00 cm
CONCENTRATION A = 0·0410 g/ℓ
B = 0·0813 g/ℓ E = 8·1803 g/ℓ
C = 0·8131 g/ℓ F = 81·305 g/ℓ
D = 4·0883 g/ℓ
LABORATORY
ANGLO-IRANIAN OIL CO. LTD
RESEARCH STATION
SUNBURY-ON-THAMES
MIDDLESEX
ENGLAND

FIG 6

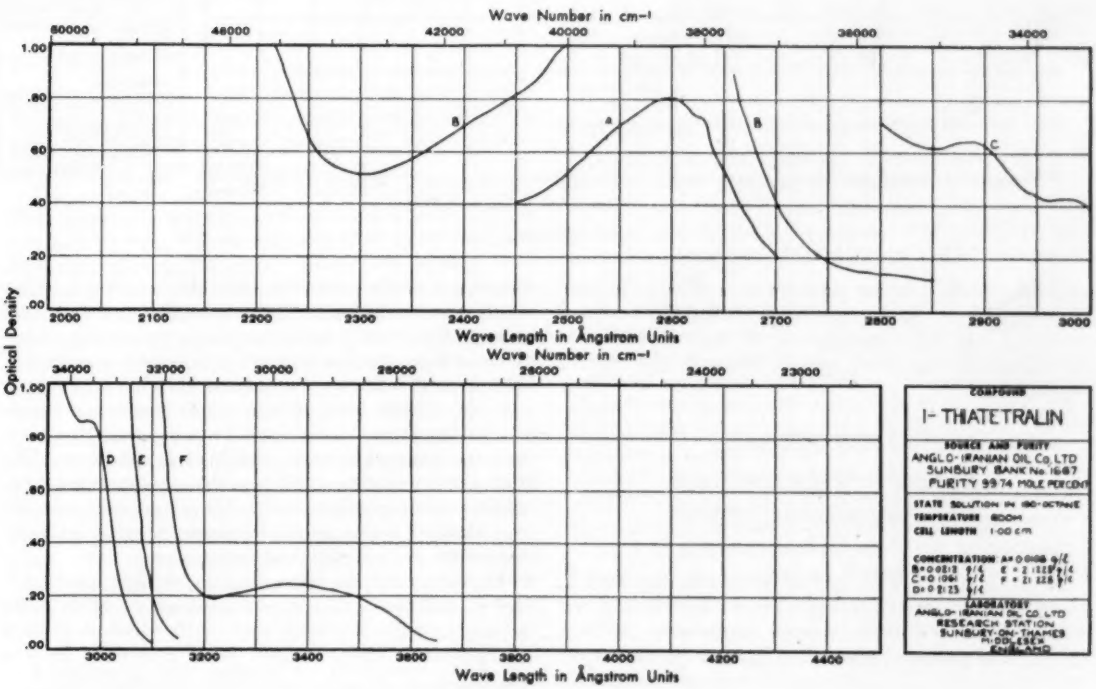

Wave Number in cm⁻¹
50000
46000
42000
40000
38000
36000
34000
1.00
.80
.60
.40
.20
.00
A
B
C
2000
2100
2200
2300
2400
2500
2600
2700
2800
2900
3000
Wave Length in Ångstrom Units
Optical Density
Wave Number in cm⁻¹
34000
32000
30000
28000
26000
24000
23000
D
E
F
3000
3200
3400
3600
3800
4000
4200
4400
Wave Length in Ångstrom Units
COMPOUND
1-THIATETRALIN
SOURCE AND PURITY
ANGLO-IRANIAN OIL Co. LTD
SUNBURY BANK No 1687
PURITY 99·74 MOLE PERCENT
STATE SOLUTION IN ISO-OCTANE
TEMPERATURE ROOM
CELL LENGTH 1·00 cm
CONCENTRATION A = 0·0108 g/ℓ
B = 0·0218 g/ℓ E = 2·1228 g/ℓ
C = 0·1096 g/ℓ F = 21·228 g/ℓ
D = 0·1123 g/ℓ
LABORATORY
ANGLO-IRANIAN OIL CO. LTD
RESEARCH STATION
SUNBURY-ON-THAMES
MIDDLESEX
ENGLAND

FIG 7

with structure. All four sulphides dissolve in the acid, giving characteristic colours. With 2-thiatetralin and 2-thiaindane action appears, however, to be mainly limited to physical solution, since the sulphide is recovered unchanged on dilution with water. With 1-thiatetralin and 1-thiaindane, however, reaction occurs, but no sulphonate could be identified, only oily or resinous products being obtained.

To obtain some indication of the relative reactivity of the individual sulphides each was heated in hydrocarbon solution with finely divided sodium to 190° C, a period of ½ hour. The product was cooled, diluted with water (1 litre), and the alcohol distilled off through a short glass-packed column until an overhead temperature of 80° C was reached. Steam distillation of the residue, using a continuous oil–water separater,* gave a pale yellow oil which was dissolved in ether, washed with 10 per cent caustic soda solution (1 litre) until free from *o*-ethyl thiophenol, then with water, and finally dried over calcium chloride. (The alcohol distilled from the original reaction product yielded a further small quantity of the sulphide, which was

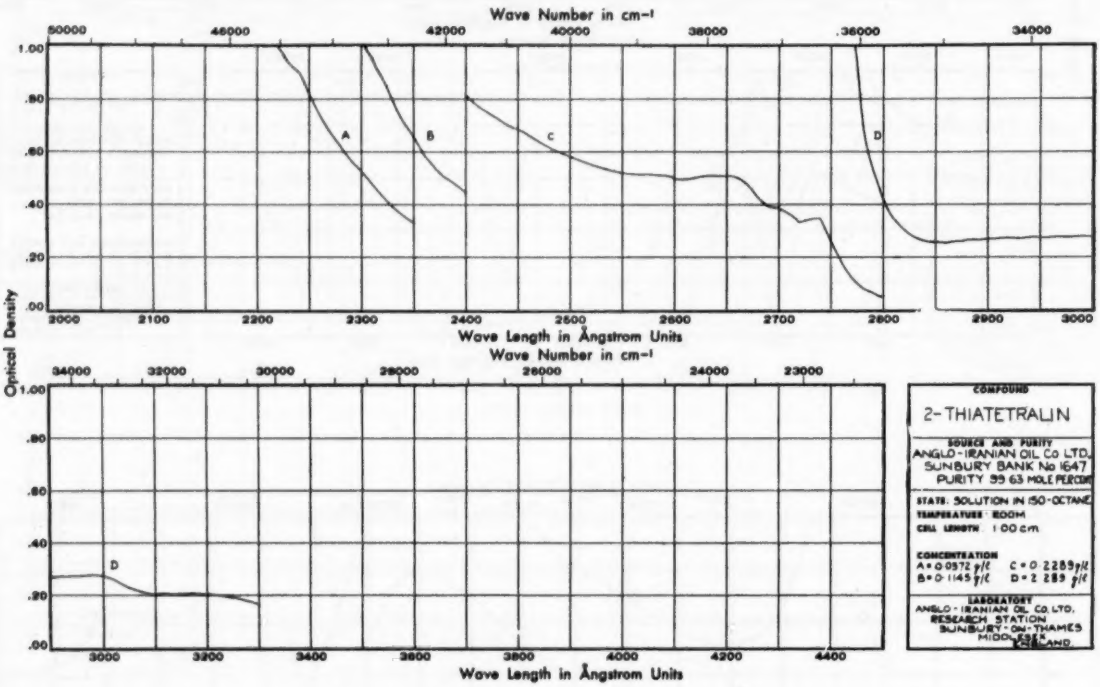


FIG 8

sufficient sodium being used for complete desulphurization. Since the extent to which sulphur removal occurred was comparable with all four sulphides, it would appear that their activity towards this reagent is similar.

EXPERIMENTAL

Analyses by Weiler and Strauss

All melting points are corrected

1-*Thiaindane*

Benzothiophene (350 g, 2·61 mol) was dissolved in absolute ethyl alcohol (2·5 litre) in a 5-litre flask fitted with a 6-ft, wide-bore copper condenser. Sodium (120 g, 5·21 g atoms) was added in three portions over recovered as the mercuric chloride complex.) After distillation under reduced pressure, the crude product (600 g) from 700 g benzothiophene, consisting of unreduced benzothiophene and 1-thiaindane, was treated with a cold solution of mercuric chloride (2800 g) in ethanol (11,000 ml). Under these conditions the 1-thiaindane formed a derivative which crystallized out, and the benzothiophene remained in solution. The derivative was filtered off, purified by crystallization, the sulphide regenerated with dilute hydrochloric acid, and distilled under reduced pressure to give 1-thiaindane (196 g), b.p. 93° C at 6 mm.

The pure sulphide, when freshly distilled, is a colourless liquid possessing a not unpleasant odour. Its behaviour with sulphuric acid, with which it gives a characteristic claret colour, is of interest. It was

* A modification of the separator described by Human and Mills [29] was employed.

completely removed from decalin solution (7 g 1-thiaindane in 50 ml decalin) on shaking with the concentrated acid (30 g) for 20 minutes, considerable sulphur dioxide formation taking place in the process. The acid layer, poured on to ice, on standing deposited neutral viscous oily drops, which were taken up in chloroform. The residue left on removal of the solvent was an odourless resinous material (3·6 g) which gave an intense blue solution with concentrated sulphuric acid.

Derivatives, other than the sulphoxides, were prepared by the methods outlined in an earlier paper.[1] The sulphoxide was prepared by the addition of a 50 per cent excess of the equivalent quantity of a solution of *tert*-butyl hydroperoxide in *tert*-butyl alcohol (active oxygen content 10 per cent) to a cooled solution of the sulphide (0·05 mol) in acetic acid (15 ml). After standing at room temperature for 24 hr, it was gently refluxed to destroy excess of peroxide. Removal of the solvent and distillation of the residual oil under reduced pressure gave the sulphoxide, which was crystallized from benzene.

1-*Thiaindane Sulphoxide* forms colourless needles, melting at 67° to 68° C (Found : C, 63·60; H, 5·73; S, 21·37; calc for C_8H_8SO : C, 63·12; H, 5·30; S, 21·06 per cent). The mercuric chloride addition compound melted at 131° to 132° C (Found : C, 14·62; H, 1·15; S, 4·64; Cl, 21·72; calc for $C_8H_8S.2HgCl_2$: C, 14·14; H, 1·18; S, 4·72; Cl, 20·88 per cent.) The sulphone melted at 90·0° to 91·3° C. (Found : C, 57·3; H, 4·91; S, 18·92; calc for $C_8H_8SO_2$: C, 57·12; H, 4·79; S, 19·06 per cent.) The methiodide was an oil.

2-*Thiaindane*

(a) o-*Xylene*. Crude *o*-xylene was fractionated through a 100-plate column and the material boiling from 144·0° to 144·4° C at 760 mm n_D^{20} 1·5048 to 1·5049 was used for the succeeding preparation.

(b) o-*Xylene dibromide* (o-*di*-(*bromethyl*)*benzene*). This dibromide was prepared by the method of Atkinson and Thorpe,[22] from *o*-xylene (400 g, 3·8 mol) and bromine (1215 g, 7·6 mol). The crude product from several batches was distilled under reduced pressure, the material boiling at 138° to 150° C at 8 mm was filtered and the solid crystallized from *iso*hexane to give the highly lachrymatory dibromide, melting point 94·3° to 95·3° C in 31 per cent yield. (Found : Br, 60·8; calc for $C_8H_8Br_2$, Br, 60·6 per cent.)

(c) 2-*Thiaindane*. 2-Thiaindane was prepared from the above dibromide (825 g, 3·1 mol) and an aqueous–alcoholic solution of sodium sulphide nonahydrate (1488 g, 6·2 mol) with a yield of 67 per cent and purified by crystallization of the mercuric chloride complex. The preparation and purification were both carried out in an atmosphere of nitrogen. Fractionation of the regenerated sulphide through a 25-plate glass-packed column under reduced pressure, yielded a fraction boiling at 106° to 107° C/9 mm, which, on redistillation *in vacuo* to remove the blue colour which tends to develop in the sulphide in the presence of air, gave the pure sulphide (169 g) as a colourless liquid solidifying on cooling. It possesses a pleasant aromatic odour similar to that of the other sulphides described in this paper.

On contact with air, the colourless solid rapidly darkens in colour, becoming converted into a deep reddish liquid which later deposits an insoluble blue amorphous solid (cf. v. Braun, Bayer, and Kaiser [7]). It was on occasion, however, observed that this oxidation was much delayed and occurred only after a very prolonged period of exposure to air in a shallow dish. The possibility that under certain conditions an inhibitor is formed which prevents further oxidation is being investigated. Attempts to isolate intermediate oxidation products by chromatography have been unsuccessful.

2-Thiaindane gives a magenta colour with sulphuric acid. It is removed from decalin solution by the concentrated acid, and may be recovered unchanged from the latter on dilution with water.

The mercuric chloride addition compound melted at 131·5° to 132·5° C. (Found : C, 35·50; H, 3·08; S, 11·69; Cl, 13·18; calc for $(C_8H_8S)_2HgCl_2$: C, 35·33; H, 2·96; S, 11·78; Cl, 13·04 per cent.) The sulphone melted at 151·3° to 151·5° C. (Found : C, 56·99; H, 4·95; S, 18·91; calc for $C_8H_8SO_2$: C, 57·12; H, 4·79; S, 19·06 per cent.) The methiodide melted at 160° to 161° C. (Found : C, 39·20; H, 3·74; calc for $C_9H_{11}SI$: C, 38·86; H, 3·99 per cent.) The sulphoxide melted at 90° C. (Found : C, 62·97; H, 5·82; S, 21·76; C_8H_8SO requires C, 63·12; H, 5·30; S, 21·06 per cent.)

1-*Thiatetralin*

(a) *Ethylene Cyanohydrin*. This was prepared in 74 per cent yield (1357 g) by the method described by Gilman and Blatt,[23] and fractionated through a 50-plate glass-helix packed column. The purified material had a boiling point of 117·5° to 118·0° C at 17 mm and n_D^{20} 1·4267.

(b) 2-*Bromopropionic Acid*. This acid was obtained in 72 per cent yield by a modification of the method described by Gilman and Blatt.[24] Hydrogen bromide, prepared by direct combination of hydrogen and bromine [25] was passed into a mixture of ethylene cyanohydrin (850 g) and water (2·1 litres) until no further increase in weight occurred (17 hr). The product was cooled to 60° C, extracted at this temperature with carbon tetrachloride, and the solid crystallized from this solvent to a constant melting point of 63° to 64° C.

(c) 2-*Phenylmercaptopropionic Acid*. This was obtained by the method of Krollpfeiffer *et al* [17] from 2-bromopropionic acid and pure thiophenol.* After

* Thiophenol was prepared by fractionation of a commercial product and had the following physical constants : b.p. 113·4° to 113·6° C at 145 mm; n_D^{20} 1·5875; d^{20} 1·0777; f.p. −15·074° C; purity 99·8 mol per cent; cryoscopic constant 2·2 mol per cent per ° C.

removal of water from the crude product by distillation with benzene the residue was crystallized to constant melting point from light petroleum ether (b.p. 40° to 60° C). 2-Phenylmercaptopropionic acid melting at 59° to 60° C. (Krollpfeiffer *et al* [17] give 59° C) was obtained in 98·4 per cent yield.

(d) 4-*Keto*-1-*thiatetralin* (4-*ketothiochroman*). Cyclization of phenylmercaptopropionic acid as described by Krollpfeiffer *et al* [17] gave the required ketone boiling at 112° to 113° C at 1·0 mm. It was obtained in 75 per cent yield after crystallization from a mixture of light petroleum ether and toluene in the ratio of 20 : 1. From the freezing point (+29·51° C) and estimated cryoscopic constant of 3·0, the purity was estimated to be 99·5 mol per cent.

(e) 1-*Thiatetralin*. 4-Keto-1-thiatetralin was reduced by Clemmensen's method using amalgamated zinc (450 g), 22 per cent hydrochloric acid (2250 ml), and ketone (137 g). The sulphide was recovered by steam-distillation, washed first with sodium bicarbonate solution and then with water, dried over calcium chloride, and distilled under reduced pressure. The yield from 804 g of ketone was 459 g (63 per cent). After purification through the mercuric chloride complex the regenerated sulphide was finally purified by crystallization from light petroleum ether (b.p. 40° to 60° C) at low temperature, followed by distillation *in vacuo* (b.p. 76° to 78° C at 1·2 mm) to remove traces of solvent. The middle fraction from this distillation was taken as the pure sulphide.

With concentrated sulphuric acid this sulphide gives an amber colour and sulphonation appears to take place. Thus when 1-thiatetralin dissolved in decalin is shaken with the acid under the conditions described for 1-thiaindane (page 76) it is completely removed from solution and no sulphide is recovered when the acid is poured on to ice; extraction of the diluted acid with chloroform and evaporation of the solvent left a resinous material (5·7 g) which gave an olive green coloration with concentrated sulphuric acid.

The mercuric chloride addition compound melted at 89° to 90·5° C. (Found : C, 26·29; H, 2·44; S, 7·78; Cl, 17·23. $C_9H_{10}SHgCl_2$ requires C, 25·63; H, 2·39; S, 7·6; Cl, 16·82 per cent.) The sulphone melted at 87° to 89° C. (Found : C, 59·57; H, 5·71; S, 17·42; calc for $C_9H_{10}SO_2$: C, 59·31; H, 5·51; S, 17·59 per cent.) The methiodide was an oil. The sulphoxide, which was extremely deliquescent, melted at approximately 31° to 34° C.

2-*Thiatetralin*

(a) *iso*Chroman. *iso*Chroman was prepared by the method of Buschmann and Michel [26] from 2-phenylethyl alcohol (610 g), concentrated hydrochloric acid (2850 g), and paraformaldehyde (165 g). The product was fractionated under reduced pressure (12 to 14 mm) through a 20-plate glass-packed column, fractions having refractive index n_D^{20} 1·5451 to 1·5453 being bulked as *iso*chroman; yield 77 per cent. The physical properties determined on a middle cut from the fractionation were : b.p. 92° C at 13 mm n_D^{20} 1·5452, d^{20} 1·0691, f.p. +3·815° C purity 99·3 mol per cent (cryoscopic content estimated to be 3·0 mol per cent per ° C).

(b) o-2-*Bromoethylbenzylbromide* (o-homo*xylylene*-*dibromide*). Hydrobromination of *iso*chroman using anhydrous hydrobromic acid [25] yielded the dibromide, b.p. 128° to 129° C/1·5 mm Hg. Crystallization from *iso*hexane gave *o*-2-bromoethylbenzylbromide in 63 per cent yield as a lachrymatory white solid melting at 52° to 54° C. (Found : Br, 56·8; calc for $C_9H_{10}Br_2$: Br, 57·6 per cent.) (Holliman and Mann [27] give m.p. 53° C.)

(c) 2-*Thiatetralin*. The dibromide (600 g, 2·15 mol) was converted to the cyclic sulphide using sodium sulphide nonahydrate (1040 g, 4·35 mol), water (944 ml), and ethanol (1180 ml), and the crude product (59 per cent yield) was purified through the mercuric chloride complex. Fractionation under reduced pressure, through a glass-packed 25-theoretical plate column gave the sulphide (165 g) as a colourless liquid boiling at 111° C at 6·5 mm to 115° C at 7·0 mm.

2-Thiatetralin is readily oxidized in the presence of air. A sample which had been stored in a corked bottle for 35 months was distilled under reduced pressure to give the sulphide b.p. 99° at 2 mm to 100° C at 3 mm, a fraction b.p. 110° at 3 mm to 180° at 4 mm which was almost entirely the sulphoxide (m.p. and mixed m.p. with an authentic specimen), and a small residue which was not identified. Chromatographic separation of the stored sulphide using an alumina column gave the unchanged sulphide (78·5 per cent) by eluting with petroleum ether and benzene, a series of fractions (totalling 16 per cent) by elution with diethyl ether-alcohol ratio 2 : 1, which were shown to be mainly the sulphoxide (m.p. and mixed m.p.) together with an unidentified oily material and a fraction (2·2 per cent) by elution with ethyl alcohol which was not identified.

With concentrated sulphuric acid, 2-thiatetralin gives a lemon yellow colour. It is completely removed from a hydrocarbon solution by the acid, under the conditions described for 2-thiaindane, and may be recovered unchanged on pouring the acid on to ice.

The mercuric chloride addition compound melted at 203·3° to 204·3° C. (Found : C, 25·59; H, 2·29; S, 7·39; Cl, 16·98; calc for $C_9H_{10}SHgCl_2$: C, 25·63; H, 2·39; S, 7·60; Cl, 16·82 per cent.)

The sulphone melted at 164° to 165·5° C. (Found : C, 59·54; H, 5·07; S, 17·86; $C_9H_{10}SO_2$ requires C, 59·32; H, 5·53; S, 17·59 per cent.) The methiodide melted at 123·2° to 123·7° C. (Found : C, 41·48; H, 4·59; S, 10·42; I, 43·26; calc for $C_{10}H_{13}SI$: C, 41·11; H, 4·48; S, 10·97; I, 43·44 per cent.)

The *sulphoxide* melted at 92° to 92·5° C. (Found : C, 65·40; H, 6·44; S, 19·4; $C_9H_{10}SO$ requires C, 65·02; H, 5·06; S, 19·28 per cent.)

ACKNOWLEDGEMENTS

We wish to thank the chairman of the Anglo-Iranian Oil Company Ltd. for permission to publish this

paper, Dr. H. Powell for spectra, J. A. Conyers for help in the synthetic work, and D. G. Barnard-Smith for determination of physical constants.

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CORRESPONDENCE

EXAMINATION OF USED LUBRICATING OILS

The Editor, *Journal of the Institute of Petroleum.*

SIR,

I have read with interest the papers presented at the Symposium on Examination of Used Lubricating Oils in the July 1953 issue of the *Journal*. I was unable to attend the meeting, but wish to make the following comments.

(*a*) In regard to Dr J. B. Matthews' paper on "The deterioration in use of the I.C. engine crankcase oils," how are the figures for "carbon" and for the $CHCl_3$-soluble fraction of oil-insolubles interpreted in the case of oils containing a large proportion of detergent additive? The detergent will be largely extracted with the oil-insolubles or perhaps remain in the "carbon." Consequently, the results will need correction, as it does not seem possible to distinguish between absorbed oxidation products and absorbed detergents.

(*b*) With reference to the paper by Brook, Matthews, and Taylor, I do not share the view that dissolved metallic compounds are the only catalysts to be considered of importance in the catalytic oxidation of lubricating oils.

Also, I do not agree that copper and iron compounds are the only active catalysts. Both solid and dissolved metals are active catalysts, and the fact that the reactive velocity drops suddenly where the solid phase is removed from the reacting liquid confirms this (*J. Inst. Petrol.*, 1952, **38**, 449). On this question reference should be made also to the action of silicates (*J. Inst. Petrol.*, 1951, **37**, 316; 1952, **38**, 445). Although some of the experiments were performed with aromatic-free oils, it is also true that in ordinary practice many facts point in the same direction. The catalytic action of silicates is employed in fluidized cracking technique, and few will accept that the only reason why dust is prevented from entering a crankcase is because of its abrasive effect.

(*c*) Reference is made in the same paper to the McKee and Fritz modification of the Stäger–Künzler test and to unpublished modification of the same test by van der Minne. In this connexion reference should be made to my own paper "Stability test of motor lubricants" (*J. Inst. Petrol.*, 1951, **37**, 316), which contains the same and also other modifications of the strip test. It does not seem possible that this paper has escaped the attention of the Thornton team, as the method has been widely accepted in several laboratories in Europe. It has also been referred to in E. G. Ellis' book "Lubricant Testing."

(*d*) Replying to a question from Mr Gossling, Mr Brook said that the strongly-detergent compound separated from the used lubricating oil had a molecular weight of 2800. This figure is interesting because it was shown (*J. Inst. Petrol.*, 1949, **35**, 88) that the molecular weight, even of "resinic" oxidation products of white oil and transformer oil, is of the same magnitude as of the original oil. If the solvent used in the molecular weight determination was benzene, I would recommend that the determination be repeated with benzophenone. It is then probable that a lower molecular weight, of the order of that of the oil itself, will be obtained. We found 1800 with benzene, 380 with dioxane, and 400 with benzophenone. Apart from molecular weight, the main point is the general trend during oxidation. This is toward constancy of molecular weight, the observed increase of viscosity being due not to polymerization but to the appearance of polar groups in the molecule.

Yours faithfully,
D. J. W. KREULEN

Rotterdam,
7 *September* 1953.

The Editor, *Journal of the Institute of Petroleum.*

SIR,

I am glad to be able to answer the questions put by Mr Kreulen in his letter and reply to his comments.

In reply to the first question (*a*), it is first necessary to point out that no attempt was made in the work described to measure the exact amounts of oxidation products, "carbon," inorganic matter, and other constituents of used oils. In order to obtain precise data of this kind, it would be necessary to embark on the development of very involved methods of analysis with little hope of complete success, because of the complex chemical and physical nature of the deterioration products. For this reason we restricted ourselves to simple measurements, which, however, could be performed accurately. In the interpretation of these quantitative data certain assumptions have to be made which introduce a qualitative element into the final conclusions. Thus, on the basis of experimental evidence, the chloroform-soluble fraction of the oil-insolubles is taken to be only "a measure" of the oil oxidation products contained in them. Again, the insoluble inorganic matter is obviously given only "to a first approximation" by the difference in the sulphated ash values of the used oil and the filtered used oil. The amount of additive which is adsorbed on the oil-insolubles is generally small compared with the quantities we are discussing, and may therefore be ignored in the simplified interpretation. The paper does not attempt to put forward a scheme of analysis for used oils, but merely to describe in general terms their nature, and how they were formed.

Turning now to the comments (*b*), according to Mr Kreulen (*J. Inst. Petrol.*, 1952, **38**, 449) amounts of metallic copper surface up to 2 cc/ml oil have almost no effect on the reaction velocity of a white oil, and it is necessary to increase the surface area to 54 cc/ml oil in order to get a mere four-fold increase on the rate

of oxidation. Such a high ratio of copper surface to oil is well outside lubricating oil field experience, so that, assuming that lubricating oils behave similarly to Mr Kreulen's white oil, one is led from his own data to the conclusion that metallic copper is of no significance in the oxidation of crankcase lubricating oils. On the other hand, in our laboratories we find that by exposing 0·25 cc of copper metal surface to 1 g oil at 160° C, the rate of oxidation of a typical lubricating oil is increased about 100-fold. Moreover, Brook and I (*Faraday Soc. Disc.*, 1951, No. 10, 298) have shown that this high catalytic activity of metallic copper can be attributed entirely to dissolved copper ion.

It is, therefore, difficult to understand why Mr Kreulen found it necessary to use such large quantities of copper to obtain any measurable catalysis. Three possible reasons suggest themselves. The first is that his white oil behaves quite differently from lubricating oils. Another is that his dipole moment changes do not measure the same thing as our oxygen absorption rates. The third is that his apparatus differs from ours in that the gaseous products of oxidation (CO_2, CO, H_2O, etc.) are not removed continuously from the reaction vessel, and may, therefore, build up to sufficiently high concentrations to seriously reduce the partial pressure, and therefore the dissolved concentration, of oxygen. It would be interesting to see some data obtained in Mr Kreulen's apparatus on the influence of soluble copper salts alone on the rate of oxidation, and on the rate of oxygen absorption. Such information is certainly necessary before his results can be usefully compared with ours.

Mr Kreulen quotes as proof of the catalytic activity of copper surfaces the fall in the reaction velocity he obtained on removing the solid phase. Before accepting this conclusion, it would be necessary to know how much dissolved copper ion was removed from the system by adsorption on the filter used for removing the metallic copper, because a reduction in the concentration of dissolved copper ion might account for the fall in the reaction velocity. Support of this alternative hypothesis is provided by Mr Kreulen's own observation that the reduction in velocity is the more marked the smaller the amount of copper surface and dissolved copper ion. It would also be instructive to know how much soluble copper ion becomes precipitated in the form of sludge in Mr Kreulen's experiments.

In Mr Kreulen's experiments on the influence of other solid phases on the oxidation rates (*J. Inst. Petrol.*, 1952, **38**, 445) it should be noted that removal of the solid phase by settling and presumably decantation did not in any case alter the rate of the oxidation, and hence a surface action does not seem to be involved. Incidentally, catalytic cracking is not the same thing as low temperature oxidation, and the silica used is not the catalyst but merely the carrier for the catalyst. I have never heard anyone suggest before that silica dust entering the crankcase can act as an oxidation catalyst.

In his comments (*c*) Mr Kreulen draws attention to certain omissions in the list of references quoted by us. The explanation of this is a simple one: when we were writing up our work, neither Mr Kreulen's paper nor Ellis' book had yet been published, and Stäger and Künzler's work which, as Mr Kreulen points out, anticipated that of McKee and Fritz, was unknown to us. This was not a case, therefore, of our having deliberately ignored anyone who has made original contributions to the subject.

Finally, with respect to question (*d*), the molecular weight value given by Mr Brook was obtained ebullioscopically in benzene and, as suggested by Mr Kreulen, it would be interesting to determine whether any degree of association occurs in this solvent. It should be noted, however, that the material separated from oxidized oil contains very few polar groups per molecule (only about two oxygen atoms per molecule and one sulphur atom shared between about six molecules if the molecular weight is only 500 according to Kreulen), that it is insoluble in acetone, and that the molecular weight is independent of concentration in benzene. All of these observations suggest that association will not occur in benzene.

Yours faithfully,
JOHN B. MATTHEWS

Thornton,
27 *November* 1953.

CORRECTION TO THE LIST OF MEMBERS

It is regretted that in the last list of members published as at November 1952

B. D. Cauthery was shown incorrectly as an Associate Member instead of a Member,

F. D. Boyle was shown incorrectly as an Associate Member instead of an Associate Fellow, and

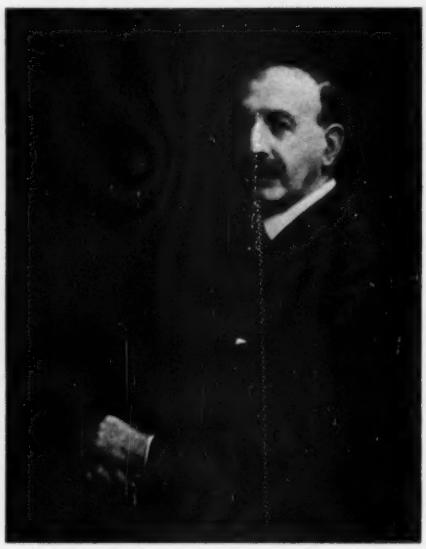
T. C. R. Baker was shown incorrectly as an Associate Fellow instead of a Fellow.

OBITUARY

SIR JOHN T. CARGILL, BART.

It is with regret that we record the death on 24 January 1954 of Sir John T. Cargill, Bart., in his eighty-eighth year.

Born in Glasgow in 1867, the second son of David Sime Cargill, a well-known East India merchant, he was educated at Glasgow Academy. At the age of nineteen he went to Rangoon as an apprentice with Finlay, Fleming and Company, managing agents of the Burmah Oil Company, which had been founded a few years previously by his father.



Returning to Glasgow after seven years in the East, during which time he had laid the foundations of a successful career and had made a study of the world's oil needs, he became his father's principal assistant. In 1905 he succeeded his father as chairman of the Burmah Oil Company, and held that position until in 1943 ill health brought about his retirement.

During his thirty-eight years as chairman of the Burmah Oil Company, Sir John saw great advances in his company, the steady development of which owed a great deal to him. It was during his chairmanship, in 1909, that the Company decided to form the Anglo-Persian (now Anglo-Iranian) Oil Company, and he remained a director of the latter company until his retirement in 1943. He was also chairman of the Assam Oil Company and of Scottish Oils Ltd., and served on the board of many other companies and in particular with those connected with the Scottish shale industry.

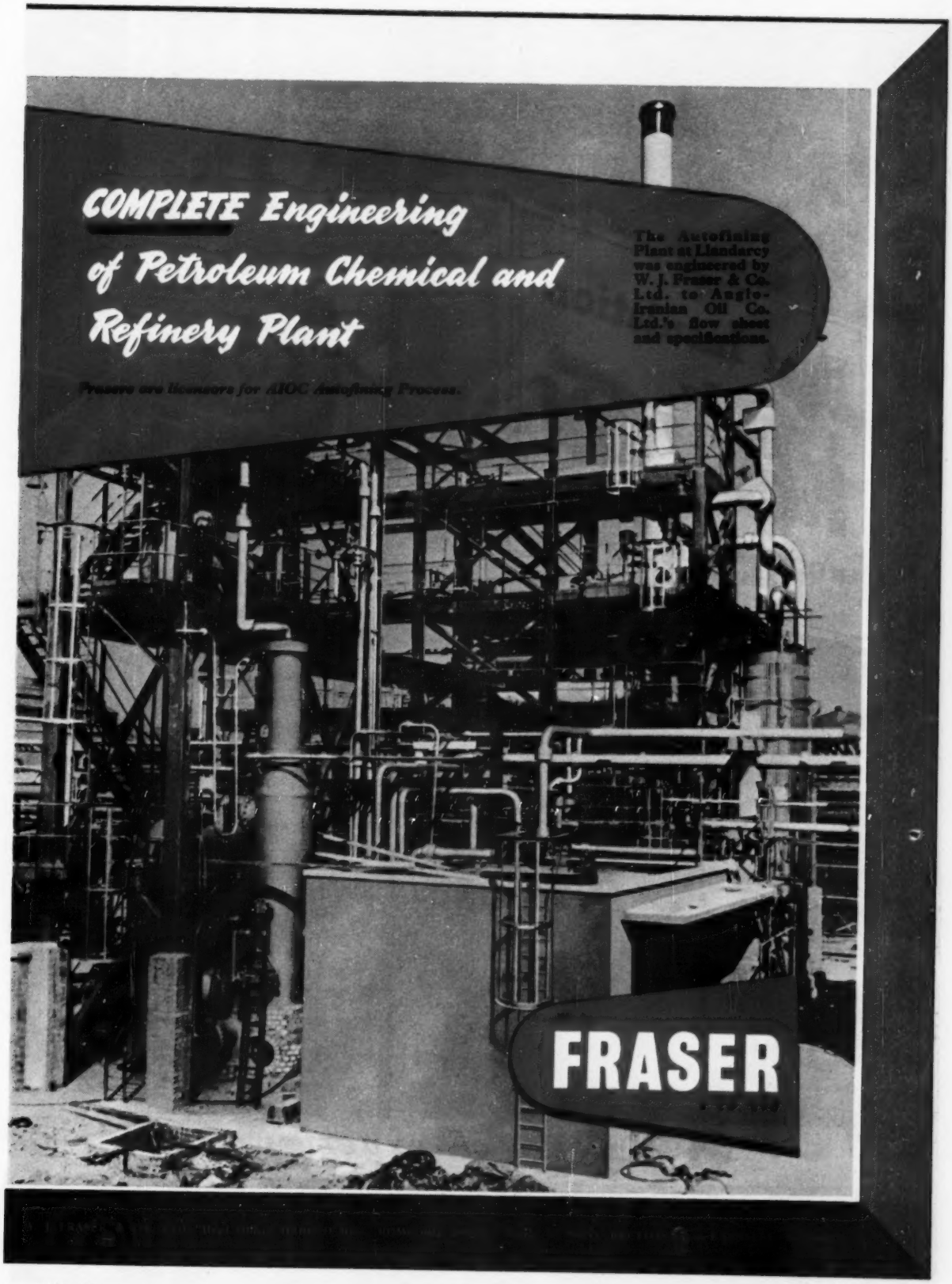
Sir John Cargill also had many business interests outside oil, and prior to his retirement had served on the boards of a number of public companies. In addition, he became a member of the Glasgow Chamber of Commerce in 1902, and in 1915 was made a director. When the Chamber formed a committee on education in 1917 he was chosen as convenor.

In 1920 he was created a baronet, and in the same year was appointed a Deputy Lieutenant of the County and City of Glasgow. The degree of LL.D. of Glasgow University was conferred upon him in 1929.

An extremely generous man, Sir John gave his benefices in a quiet and unobtrusive manner. They included, in 1920 a sum of £20,000 to found the Cargill Chair of Applied Physics at Glasgow University, in 1927, a lakh of rupees to the Rangoon University Endowment Fund, in 1930 a gift of £5000 to the Canal Boatman's Friend Society, Glasgow, in 1933 a sum of £5000 in memory of his wife, who had died in 1929, to provide X-ray equipment for Glasgow Western Infirmary.

Sir John Cargill was one of those who took a leading part in the formation of the Institute as the Institution of Petroleum Technologists. He was one of those who signed the original Articles of Association on 8 April 1914 and was included in these Articles as a Founder Member. He was elected a Member of the First Council of the Institution and remained on the Council until the end of the 1933–34 Session. During this period he served as a Vice-President from 1923 to 1933.

He is survived by his daughter.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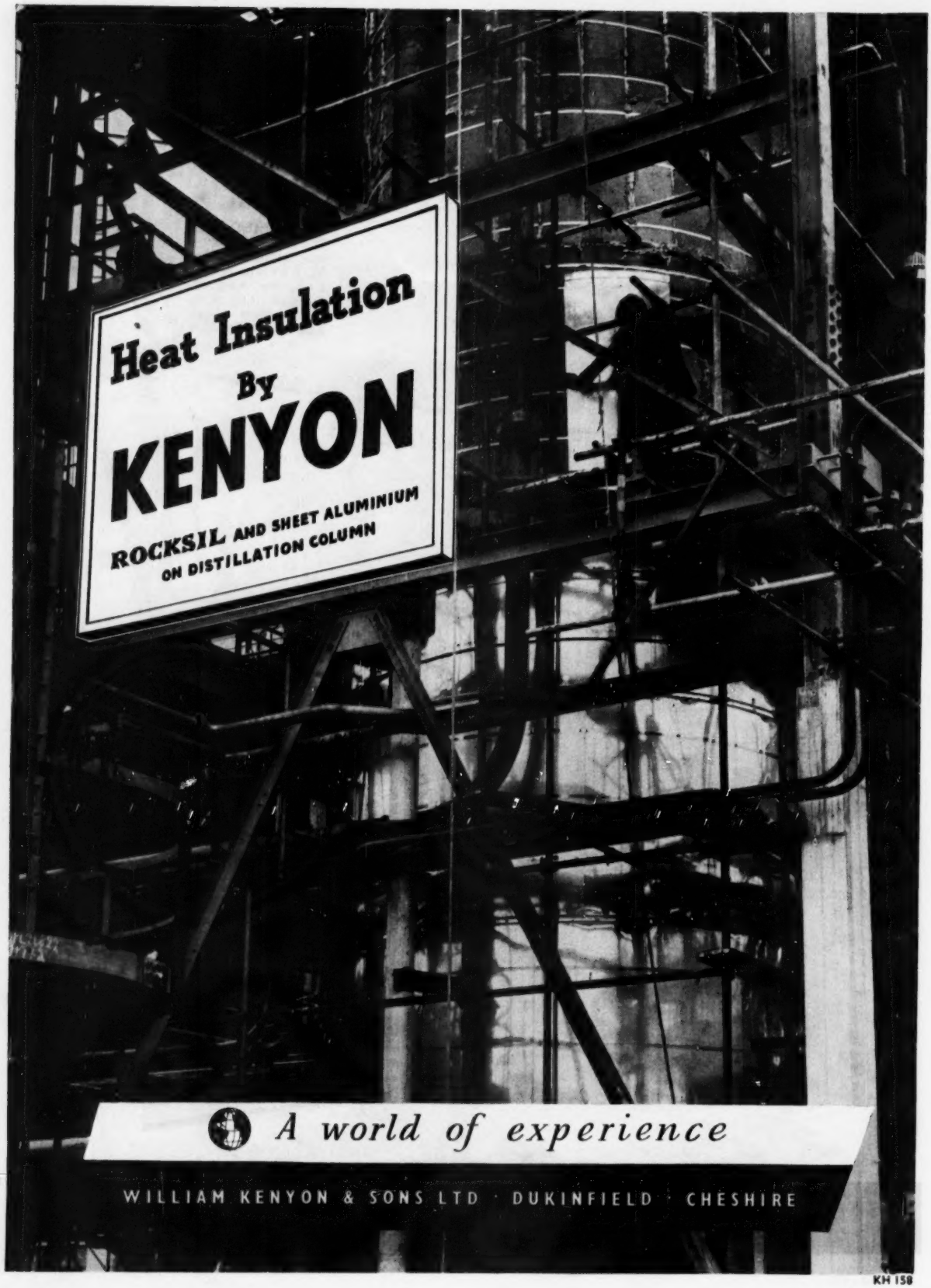
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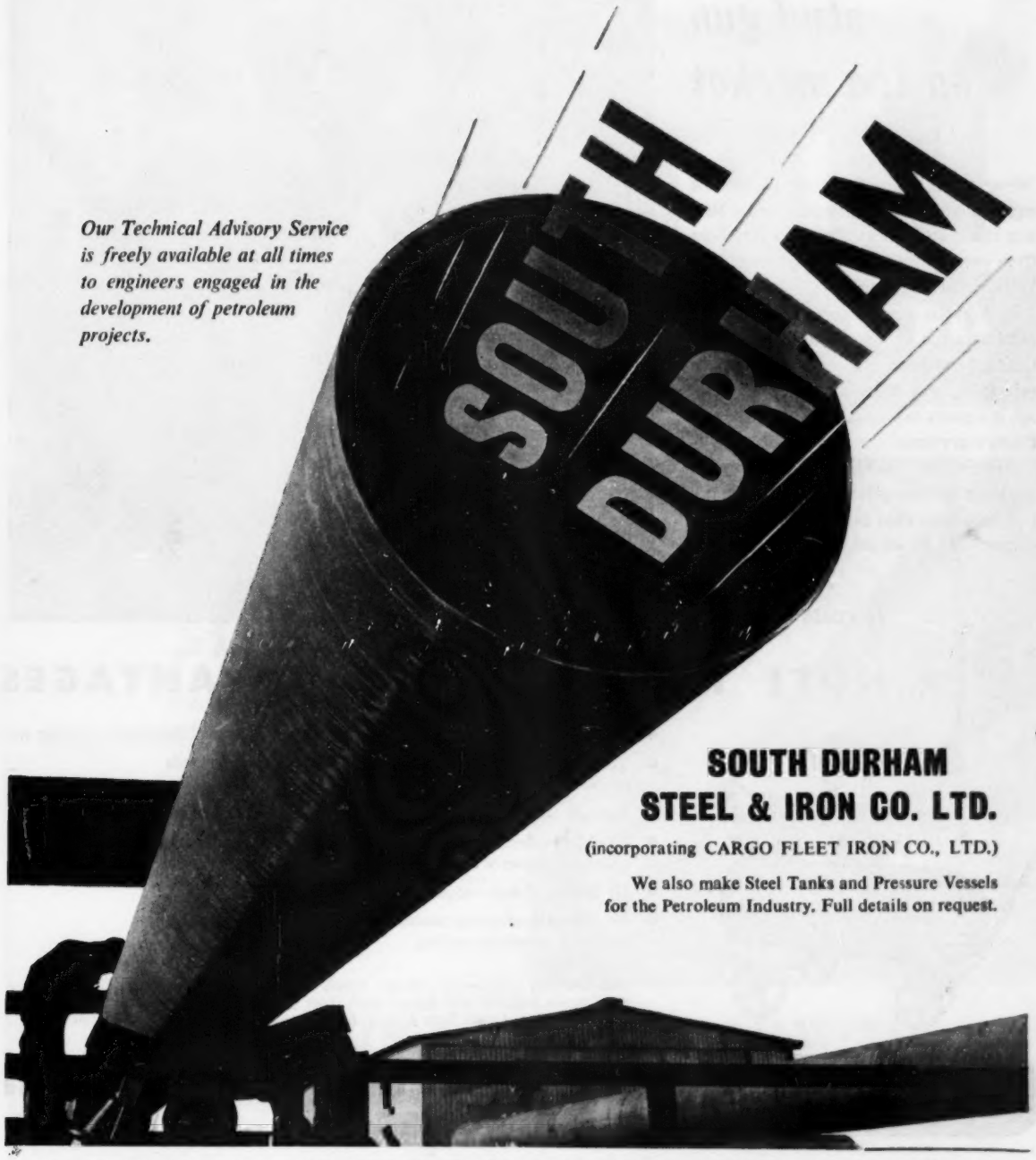

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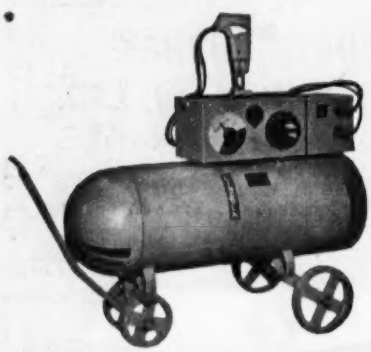

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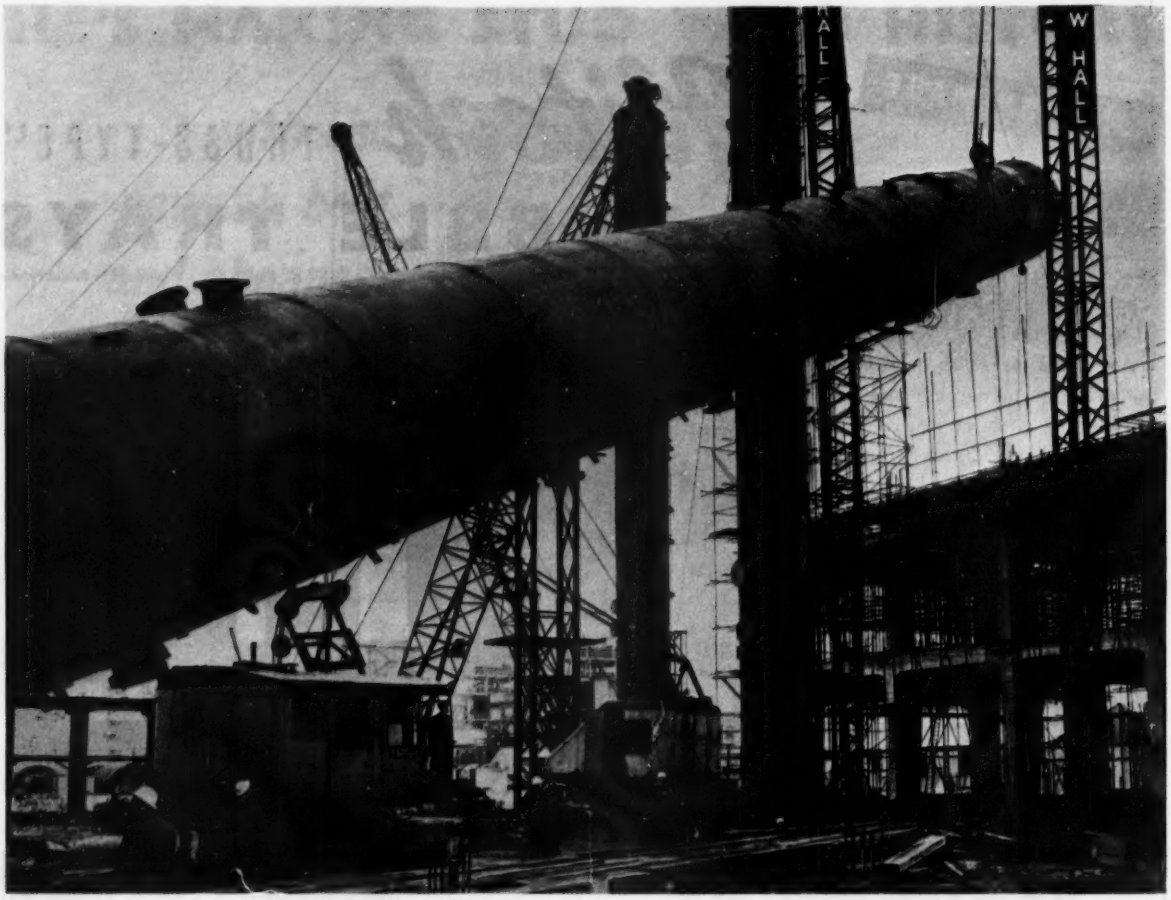

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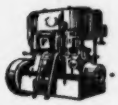

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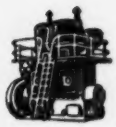

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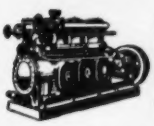

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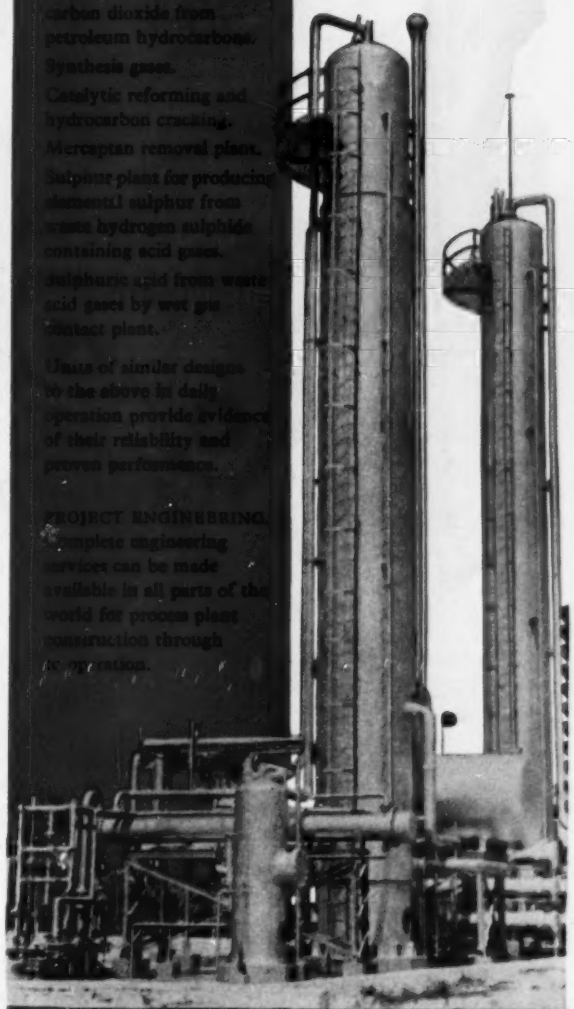

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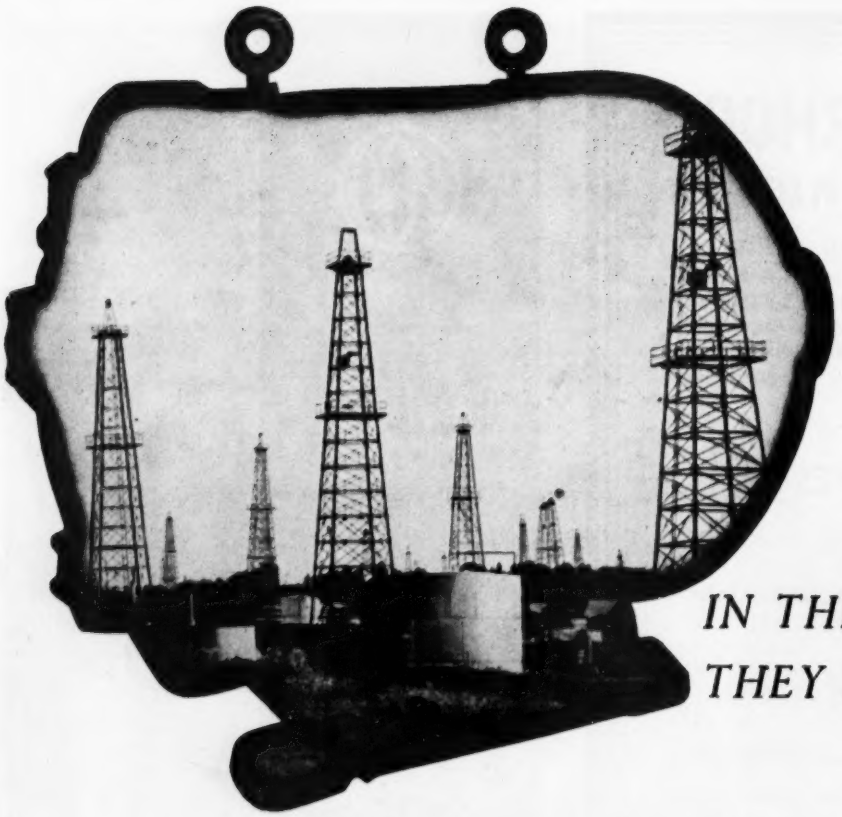

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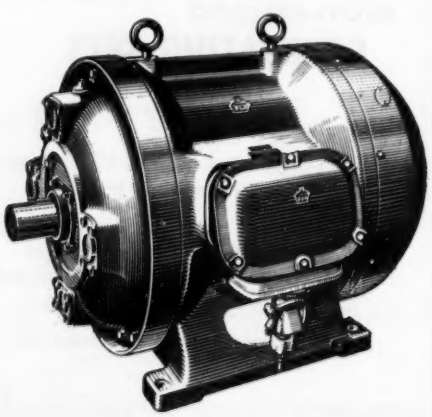

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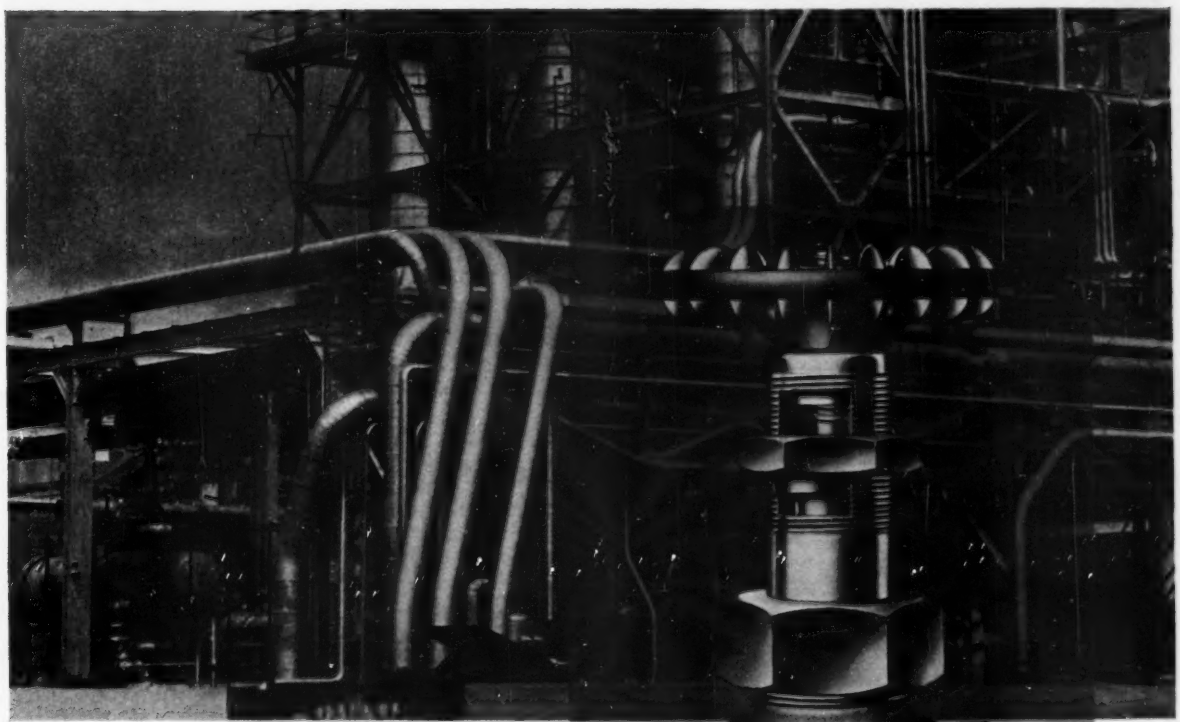

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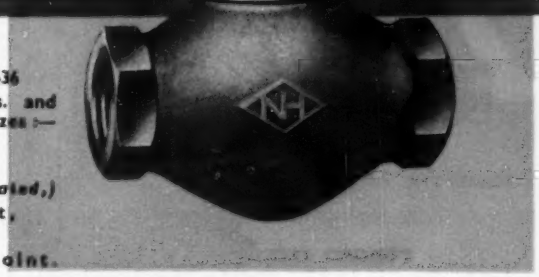

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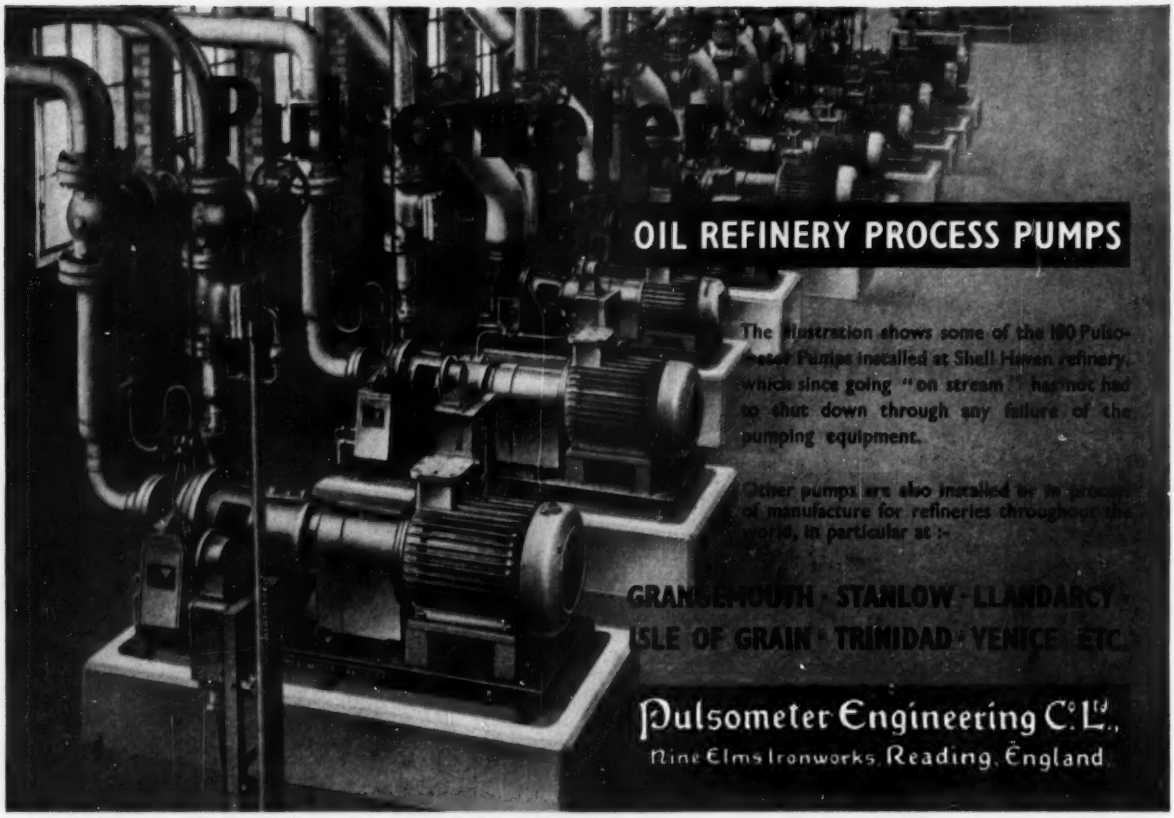
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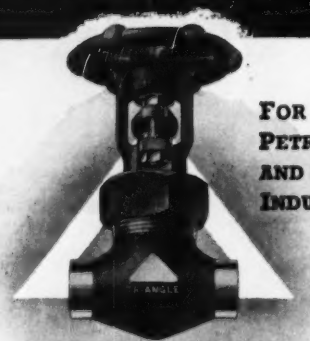

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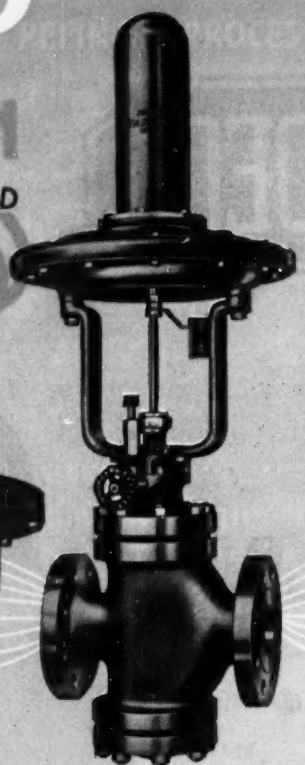

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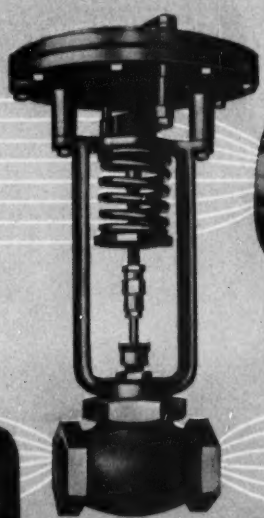

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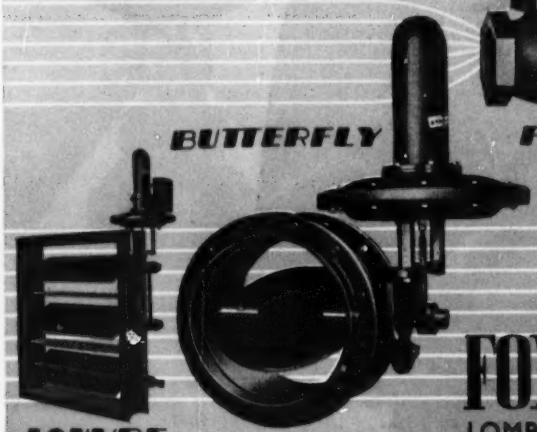

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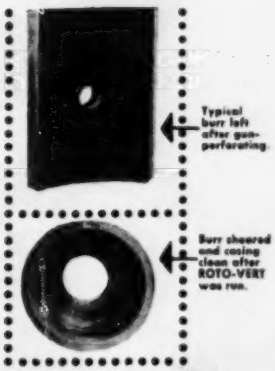

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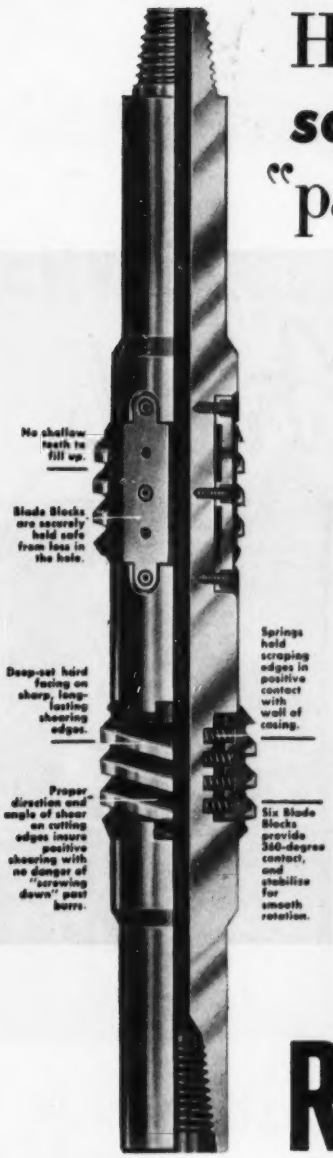
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Blade Blocks are securely held safe from loss in the hole.
Springs hold scraping edges in positive contact with wall of casing.
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Proper direction and angle of shear on cutting edges insure positive shearing with no danger of "screwing down" past burrs.
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The Baker Model "C" ROTO-VERT Casing Scraper removes undesirable obstructions from the inside of the casing, leaving it clean and smooth. Burrs or imbedded bullets are sheared away; cement, mud and scale are scraped away, so that any down-hole work can be safely done at once, or during the years to come.

SCRAPE WHILE DRILLING OUT

The ideal time to use the ROTO-VERT Casing Scraper is during the drilling out of cement, at which time it is run as a "follow-up" behind the bit. Thus in a single run you can also remove all hardened cement, mud, burrs and scale which might later damage swabs or testers, and cause packers or retainers to set prematurely—or never set at all.

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The Baker ROTO-VERT Casing Scraper is simple to run, and will effectively clean the inside of the casing *when either rotated or reciprocated* (vertical action) The low cost is paid for many times over by freedom from future damage to bailers, swab rubbers and packers, as well as by the elimination of future delays and re-running expense.

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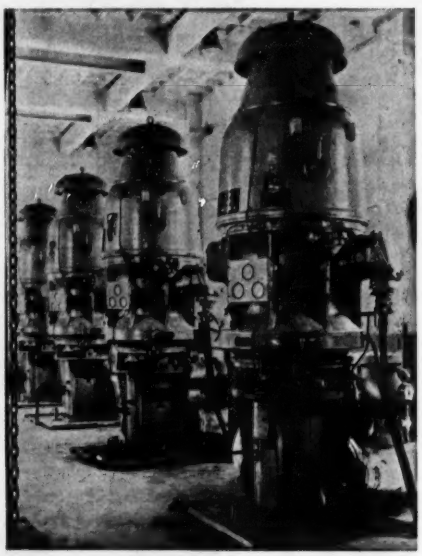

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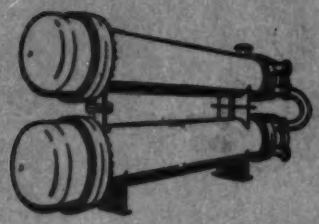

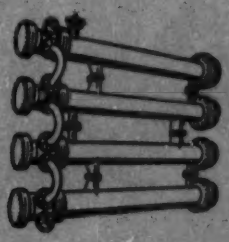

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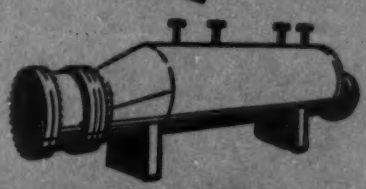

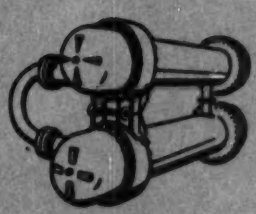

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